

Finally, the spontaneous moments seem to be associated with the cubic phase. These moments are actually induced moments that disappear when the external magnetic field is removed. The small moments observed in samples of $Cs_{0.525}VF_3$ and $Cs_{0.55}VF_3$ are probably a measure of crystal defects in those phases.

Magnetic Behavior in Rb_xVF_3 . The distortion of the orthorhombic phase from cubic symmetry is much larger in Rb_xVF_3 than in Cs_xVF_3 , although its origin is the same—namely, from ionic ordering. This distortion in Rb_xVF_3 is not simple as in Cs_xVF_3 but involves moving V and probably F to positions of lower symmetry. This change in the packing structure is reflected in the magnetic properties of Rb_xVF_3 .

As in Cs_xVF_3 , the values of C_M indicate V^{3+} orbital moments are partially quenched in the cubic phase and totally quenched in the orthorhombic phase of Rb_xVF_3 . The Θ values in Rb_xVF_3 change significantly with composition. In $Rb_{0.45}VF_3$ a considerable amount of the cubic phase is present. As in Cs_xVF_3 , delocalization in cubic Rb_xVF_3 makes a contribution to the magnetic interactions that all but cancels the antiferromagnetic contribution made by correlation effects. In the orthorhombic phase of Rb_xVF_3 , however, distortion of the V and F ions significantly reduces the extent of delocalization; hence, Θ values become considerably more negative.

The T_N values of Rb_xVF_3 are quite explicitly defined by plots of σ vs. T shown in Figure 3. Interestingly, T_N varies with x . This is again related to the changes in magnetic interactions, which involve both ferromagnetic and antiferromagnetic components. Apparently, the decrease in the ferromagnetic component reduces the total ordering energy, resulting in T_N values ~ 5 K. The magnetically ordered states of both Rb_xVF_3 and Cs_xVF_3 are antiferromagnetic overall. An analysis of the ordering would require a knowledge of the ordered structure, which could only be obtained by neutron diffraction. It is certain that the ordered structure is complex as there exist two constraints to magnetic ordering per V atom. The ordered structure, therefore, is a frustrated one in which magnetic moments are forced antiparallel to directions preferred by some of their nearest-neighbor interactions.

Finally, there appears to be small spontaneous moments associated with the cubic phase in Rb_xVF_3 , as in Cs_xVF_3 . The moments in Rb_xVF_3 are smaller than those in Cs_xVF_3 and decrease to about $0.02 \mu_B$ at $x = 0.50$, as they did in Cs_xVF_3 .

At $x = 0.55$, the moment increases again, which is probably a measure of structural defects.

Conclusions. In both Rb_xVF_3 and Cs_xVF_3 systems, the magnetic data support X-ray and optical results and the conclusions regarding V^{2+} - V^{3+} ionic ordering. In the paramagnetic region (above ~ 30 K), C_M values indicate the orbital moment is partially quenched in the cubic phase but totally quenched in the orthorhombic. The Θ values support the conclusion that delocalization (ferromagnetic contribution) as well as correlation (antiferromagnetic contribution) is involved in the magnetic exchange mechanism. Delocalization is optimized in the cubic phase. In Cs_xVF_3 , orthorhombic distortion is small and delocalization is decreased only slightly; but in Rb_xVF_3 , the orthorhombic distortion considerably reduces delocalization as seen by the significant change in Θ . The T_N values in Cs_xVF_3 are invariant because atomic positions are not significantly altered by ionic ordering, so correlation and delocalization remain in balance. The Rb_xVF_3 system, however, reflects an imbalance of these effects in its orthorhombic phase as delocalization becomes reduced. At temperatures below T_N small induced magnetic moments are associated with the cubic phase, which further supports the conclusion that V^{2+} and V^{3+} are random in this phase.

Electronic ordering has been found in the pseudohexagonal A_xVF_3 phases,^{2a} in the tetragonal K_xVF_3 phase,^{2b} and now in the modified pyrochlore A_xVF_3 phases. It appears that electronic ordering in mixed V^{2+} - V^{3+} fluoride systems is the rule rather than the exception.

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Registry No. Rb_xVF_3 , 63774-72-1; Cs_xVF_3 , 63774-59-4.

Supplementary Material Available: Guinier-Hägg X-ray data for the modified pyrochlore $Rb_{0.50}VF_3$ (Table II) and the modified pyrochlore system Cs_xVF_3 (Table III) (7 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611

Dynamic Jahn-Teller Effect in a Manganese(III) Complex. Synthesis and Structure of Hexakis(urea)manganese(III) Perchlorate

HOSSEIN AGHABOZORG, GUS J. PALENIK, R. CARL STOUFER,* and J. SUMMERS

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Hexakis(urea)manganese(III) perchlorate, $[Mn(urea)_6](ClO_4)_3$, crystallizes in the space group $R\bar{3}c$ with $a = 18.124$ (4) Å, $c = 14.042$ (3) Å, and 6 molecules/unit cell. The cation has site symmetry $\bar{3}$, which requires the six Mn-O bonds to be equivalent in an apparent violation of the Jahn-Teller theorem. The Mn-O distance of 1.986 (7) Å is virtually identical with the average value found in various distorted high-spin Mn(III) complexes. An analysis of the mean-square displacements and the visible absorption spectral data is in agreement with the existence of a dynamic Jahn-Teller effect in the cation. The Jahn-Teller radius is estimated to be about 0.33 Å, with a stabilization energy of about 36 kJ.

Introduction

Whenever the subject of the Jahn-Teller effect arises, frequent reference is made to high-spin manganese(III).^{1,2}

The majority of the octahedral complexes of this d^4 ion are high spin with magnetic moments near the spin-only value;

(1) The reference to Jahn-Teller distortion for six-coordinate, high-spin d^4 ions is found in most inorganic texts. Three common texts containing such a reference are cited in ref 2.

(2) (a) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 680. (b) Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; Saunders: Philadelphia, 1977; p 553. (c) Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978; p 378.

accordingly these complexes are expected to show a "pronounced distortion" as a consequence of the orbital degeneracy in the e_g states.³ Indeed, some of the complexes containing aromatic, N-heterocyclic ligands may be high spin because the axial distortions make the complex resistant to spin pairing. Average magnetic susceptibility data are of little value in identifying Jahn-Teller distortions since the difference is a nonmagnetic (orbital) doublet ground term for the regular octahedral complex vs. an orbital singlet for the distorted complex. Whereas the undistorted complex can have an orbital contribution via spin-orbit coupling serving to mix in excited states, the effect should be slight. More detailed magnetic data—in the form of electron spin resonance or single-crystal magnetic susceptibility results—are very limited.

Manganese(III) complexes have not been well characterized compared to many of the other tripositive, first-row transition elements. The factors responsible for the lack of data on manganese(III) complexes include its strength as an oxidizing agent, the tendency for photolytic instability³ in many cases, and the propensity for the commercially available fluoride and acetate to form mixed-ligand complexes. However, a carefully documented and reasoned interpretation of the visible spectral data for a number of manganese(III) complexes has been presented.⁴ The authors noted that the presence of two prominent bands lying between 5×10^3 and 25×10^3 cm^{-1} —and sometimes a third, which may lie within the envelope of the higher energy absorption, sometimes appearing as a shoulder upon it—is most easily rationalized as arising from the transitions ${}^5B_{1g} \rightarrow {}^5A_{1g}$ and the ${}^5B_{1g} \rightarrow {}^5B_{2g}$, respectively; the shoulder they assigned to the ${}^5B_{1g} \rightarrow {}^5E_g$ transition. These term levels arise from a splitting of the octahedral terms by a Jahn-Teller distortion. The splitting of the ground octahedral term (5E_g) is greater than that of the excited term (${}^5T_{2g}$).⁴ In this respect then, the high-spin manganese(III) systems are entirely analogous to the copper(II) systems for which there are a plethora of supporting data⁵⁻¹³ and to the high-spin chromium(II)^{4,14,15} and low-spin cobalt(II)¹⁶ systems for which there are substantially fewer data.

Contrary to the early prediction of an axial-compression manifestation of the Jahn-Teller effect,¹⁷ axial elongation appears to be the most common distortion for six-coordinate, "octahedral" complexes.^{8,10} The classic, oft-quoted reluctance of copper(II) and chromium(II) to add a third bidentate ligand to the coordination sphere is taken as evidence of Jahn-Teller distortion.¹⁸⁻²¹ Numerous X-ray diffraction studies, partic-

Table I. Crystal Data for $\text{Mn}[\text{OC}(\text{NH}_2)_2]_6(\text{ClO}_4)_3$

formula	$\text{C}_6\text{H}_{24}\text{O}_{18}\text{N}_{12}\text{Cl}_3\text{Mn}$
mol wt	713.62
space group	$R\bar{3}c$
a , Å	18.124 (4)
b , Å	18.124 (4)
c , Å	14.042 (3)
α , deg	90 ^a
β , deg	90 ^a
γ , deg	120 ^a
vol, Å ³	3995 (1)
Z	6
D_m , g cm^{-3}	1.788
D_c , g cm^{-3}	1.780
cryst size, mm	0.14 × 0.12 × 0.12
μ , cm^{-1}	8.7
radiation used	Mo $K\alpha$ -graphite monochromator
2θ range, deg	0-45
no. of measd reflcns	642
no. of reliable reflcns	364
K [in $I \approx K(\sigma(I))$]	2.0
goodness of fit	0.98
R	0.055

^a Required by symmetry of space group.

ularly for copper(II) complexes, which frequently have axial elongations, are interpreted in terms of the Jahn-Teller effect.^{8,10}

Indeed, there are a significant number of structures reported for manganese(III)²²⁻³¹ complexes that purport to demonstrate the existence of an axial distortion. The tris(acetylacetonato)manganese(III) that appeared to present an enigma later was demonstrated to be a case of mistaken identity.²⁶ But the structural data reported for the manganese(III) complexes are not for systems that are as free from additional variables as one might like. In the majority of instances, the complexes investigated contain polydentate ligands, in which instance there are inherent constraints imposed upon the nature and extent of the distortion permitted. No X-ray data are reported for mononuclear manganese(III) complexes containing only identical, monofunctional ligands. Only in such a system can one expect to observe the full extent of a structural distortion and the attendant large spectral splitting.

Although the selection of a manganese(III) complex containing but one kind of monofunctional ligand is not trivial, a suitable candidate seemed to be the complex $\text{Mn}(\text{urea})_6(\text{ClO}_4)_3$, which we have used over a period of years as a reagent in the synthesis of a variety of manganese(III) complexes.³² The hexakis(urea)manganese(III) complex is reasonably stable in the absence of moisture, it does not seem to be subject to photodecomposition, and it is easily prepared. On the basis of solution, diffuse reflectance, and mull spectra data, this complex seems to be typically distorted.³² However, the structures of the anhydrous hexakis(urea) complexes of titanium(III),³³⁻³⁵ vanadium(III),³⁶ and aluminum(III)³⁷ have

- (3) Harriman, A. *Coord. Chem. Rev.* **1979**, *28*, 147.
- (4) Davis, T. S.; Fackler, J. P.; Weeks, M. J. *Inorg. Chem.* **1968**, *7*, 1994.
- (5) Bleaney, B.; Ingram, D. J. E. *Proc. Phys. Soc., London, Sect. A* **1950**, *63*, 408.
- (6) Abragam, A.; Pryce, M. H. L. *Proc. Phys. Soc., London, Sect. A* **1950**, *63*, 409.
- (7) Bleaney, B.; Bowers, K. D. *Proc. Phys. Soc., London, Sect. A* **1952**, *65*, 667.
- (8) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143 and references therein.
- (9) Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1196.
- (10) Hathaway, B. J.; Duggan, M.; Murphy, A.; Mullane, J.; Power, C.; Walsh, A.; Walsh, B. *Coord. Chem. Rev.* **1981**, *36*, 267 and references therein.
- (11) Bertini, I.; Gatteschi, D.; Scozzafava, A. *Inorg. Chem.* **1977**, *16*, 1973.
- (12) Bertini, I.; Dapporto, P.; Gatteschi, D.; Scozzafava, A. *J. Chem. Soc., Dalton Trans.* **1979**, 1409.
- (13) Joesten, M. D.; Takagi, S.; Lenhart, P. G. *Inorg. Chem.* **1977**, *16*, 2680.
- (14) Jack, K. H.; Maitland, R. *Proc. Chem. Soc., London* **1957**, 232.
- (15) Fackler, J. P.; Holah, D. G. *Inorg. Chem.* **1965**, *4*, 954.
- (16) Bertrand, J. A.; Carpenter, D. A.; Kalyanaraman, A. R. *Inorg. Chim. Acta* **1971**, *5*, 113.
- (17) Liehr, A. D.; Ballhausen, C. J. *Ann. Phys. (N.Y.)* **1958**, *3*, 304.
- (18) Poulsen, I.; Bjerrum, J. *Acta Chem. Scand.* **1955**, *9*, 1407.
- (19) Pecsok, R. L.; Bjerrum, J. *Acta Chem. Scand.* **1957**, *11*, 1419.
- (20) Schwarzenbach, G.; Anderegg, G.; Schneider, W.; Senn, H. *Helv. Chim. Acta* **1955**, *38*, 1147.

- (21) Tichane, R. M.; Bennett, W. E. *J. Am. Chem. Soc.* **1957**, *79*, 1293.
- (22) Bartlett, M.; Palenik, G. J. *J. Chem. Soc. D* **1970**, 416.
- (23) Plaksin, P. M.; Stouffer, R. C.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 2121.
- (24) Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1883.
- (25) Avdeef, A.; Costamagna, J. A.; Fackler, J. P. *Inorg. Chem.* **1974**, *13*, 1854.
- (26) Fackler, J. P.; Avdeef, A. *Inorg. Chem.* **1974**, *13*, 1864.
- (27) Butcher, R. J.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1975**, 2517.
- (28) Matuszewski, T. L. J.; Jezowska-Trzebiatowska, B. *Acta Crystallogr., Sect. B* **1977**, *B33*, 1943.
- (29) Stults, B. R.; Day, R. O.; Marianelli, R. S.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 1847.
- (30) Stults, B. R.; Marianelli, R. S.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 1853.
- (31) Lis, T.; Matuszewski, J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1938.
- (32) Summers, J. C. Ph.D. Dissertation, University of Florida, Gainesville, FL, 1968.
- (33) Davis, P. H.; Wood, J. S. *Inorg. Chem.* **1970**, *9*, 1111.

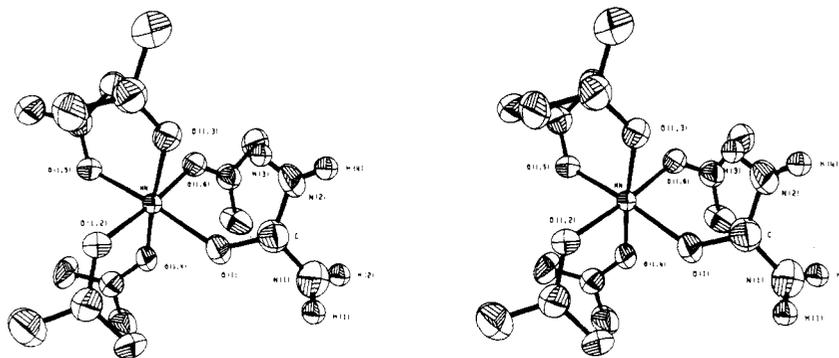


Figure 1. Stereoscopic view of the $[\text{Mn}(\text{urea})_6]^{3+}$ cation showing the atomic numbering and the thermal ellipsoids (50% probability level). Hydrogen atoms are shown for only one urea. The other hydrogen atoms are omitted for clarity.

been reported to be essentially identical ($R\bar{3}c$). This structure requiring a symmetrical molecule, i.e., equivalence of M–O distances, would be incompatible with a Jahn–Teller distorted complex. These considerations and the absence of reported structure data for the hexakis(urea)manganese(III) complex have prompted the preparation and study of this interesting ion.

Experimental Section

Preparation of Hexakis(urea)manganese(III) Perchlorate. Powdered manganese (10.0 g, 0.182 mol) was added to 400 mL of refluxing glacial acetic acid. The manganese slowly dissolved in the stirred solution over about 4 h. To the hot, stirred suspension of manganese(II) acetate was added KMnO_4 (6.5 g, 0.041 mol). After 25 min, perchloric acid (250 mL of 60% acid) saturated with urea was added to the warm, dark red solution. A dark purple microcrystalline solid formed immediately and was separated by filtration, washed with 50% (v/v) absolute ethanol–dry ether, and placed in a desiccator over CaCl_2 . The yield was 80% on the basis of the KMnO_4 used. Anal. Calcd for $\text{MnC}_6\text{N}_{12}\text{H}_{24}\text{Cl}_3\text{O}_{18}$: C, 10.10; H, 3.39; N, 23.55. Found: C, 9.67; H, 3.66; N, 22.66.

Single crystals were grown from a hot solution of 60% perchloric acid nearly saturated with urea at room temperature. The complex is insoluble in this solution at room temperature, but a small quantity dissolves at 75–80 °C. Slow cooling of the solution in a Dewar over a period of 24 h gave suitable single crystals. The crystalline complex decomposes in a few days in room air or in the X-ray beam. This decomposition is presumably caused by water vapor since the complex decomposes quickly in water.

Magnetic Measurements. The Gouy method was used to measure the magnetic susceptibility of the complex. The magnetic susceptibility is $5.02 \mu_B$ corresponding to a high-spin d^4 ion (spin-only value $4.90 \mu_B$). The $\text{Hg}[\text{Co}(\text{NCS})_4]$ complex was used as a standard.

Data Collection and Refinement. Preliminary photographs indicated that the space group was either $R\bar{3}c$ or $R3c$. The complex appeared to be isomorphous with the corresponding Ti(III) derivative.³⁴ The unit cell dimensions reported in Table I and the intensity data were measured by using a Syntex P1 diffractometer. The pertinent crystal data, together with some details of the intensity measurements, are given in Table I. The θ – 2θ scan technique with a scan rate of $12^\circ/\text{min}$ was used in measuring the intensity. The rather fast scan was used because crystal decomposition had occurred on a previous crystal. Four standard reflections were measured after every 96 reflections and were used to correct for a 6% decrease in their intensities during the course of the data collection. Absorption corrections were not made because of the small value of μ and the size of the crystal.

Structure Determination and Refinement. The final positional parameters from the isomorphous titanium complex were used as starting values for an isotropic refinement. After three cycles the R value ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) was 0.098. Anisotropic thermal refinement gave an R of 0.068 after three cycles. A difference Fourier

Table II. Final Positional Parameters ($\times 10^4$) for $\text{Mn}[\text{OC}(\text{NH}_2)_2]_6(\text{ClO}_4)_3$ with Esd's in Parentheses

	x	y	z
Mn	0 ^a	0 ^a	2500 ^a
Cl	3685 (2)	0 ^a	2500 ^a
O(1)	1040 (4)	569 (4)	1698 (5)
O(2)	3568 (6)	585 (5)	3004 (7)
O(3)	4163 (11)	612 (10)	1567 (14)
O(4)	4466 (14)	216 (25)	2276 (29)
N(1)	2334 (5)	923 (6)	1159 (9)
N(2)	1325 (6)	–473 (6)	1287 (8)
C	1549 (7)	329 (7)	1374 (8)

^a Position required by the space group symmetry.

Table III. Bond Distances (in Å) for $\text{Mn}[\text{OC}(\text{NH}_2)_2]_6(\text{ClO}_4)_3$ with Esd's in Parentheses

Cation			
Mn–O(1)	1.986 (7)	C–N(1)	1.320 (16)
O(1)–C	1.283 (15)	C–N(2)	1.305 (14)
Perchlorate Ion			
Cl–O(2)	1.38 (1)	Cl–O(4)	1.30 (3)
Cl–O(3)	1.66 (2)		

Table IV. Bond Angles (in Deg) in $\text{Mn}[\text{OC}(\text{NH}_2)_2]_6(\text{ClO}_4)_3$ with Esd's in Parentheses

Cation			
O(1)–Mn–O(1,2)	91.0 (3)	N(1)–C–N(2)	119.7 (11)
O(1)–Mn–O(1,4)	85.5 (3)	H(1)–N(1)–C	111
O(1)–Mn–O(1,5)	174.9 (3)	H(2)–N(1)–C	126
O(1)–Mn–O(1,6)	92.8 (3)	H(1)–N(1)–H(2)	117
Mn–O(1)–C	133.0 (7)	H(3)–N(2)–C	112
O(1)–C–N(1)	118.0 (11)	H(4)–N(2)–C	126
O(1)–C–N(2)	122.3 (11)	H(3)–N(2)–H(4)	120
Perchlorate Ion			
O(2)–Cl–O(2')	114.7 (6)	O(2')–Cl–O(3')	96.9 (8)
O(2)–Cl–O(3')	94.7 (8)	O(2')–Cl–O(4)	123.6 (17)
O(2)–Cl–O(4)	117.1 (17)	O(3')–Cl–O(4)	99.6 (18)

synthesis gave reasonable positions for the four hydrogen atoms. The contribution of the hydrogen atoms was included in subsequent least-squares cycles, but the positional and thermal parameters were not varied. After three cycles the final R was 0.055 and the shifts were much less than the estimated standard deviations so that the refinement was terminated. The weighting scheme was $w = 1.5 / (\sigma(F))^2$ where $(\sigma(F))^2 = [\sigma(I) + 0.04(\sigma(I))] [Lp \text{ corrections}]$. The Lp correction was calculated with the assumption of a 50% perfect and 50% mosaic graphite monochromator.

The scattering factors were taken from the usual sources.³⁸ All calculations were carried out on an Amdahl 470/V6 using local programs written or modified by G.J.P. The final positional parameters for the non-hydrogen atoms are given in Table II with the bond

(34) Figgis, B. N.; Wadley, L. G. B.; Graham, J. *Acta Crystallogr., Sect B* 1972, B28, 187.

(35) Figgis, B. N.; Wadley, G. B. *Aust. J. Chem.* 1972, 25, 2233.

(36) Figgis, B. N.; Wadley, G. B. *J. Chem. Soc., Dalton Trans.* 1972, 2182.

(37) Mooy, J. H. M.; Krieger, W.; Heijdenrijk, D.; Stam, C. H. *Chem. Phys. Lett.* 1974, 29 (2), 179.

(38) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table V. Hydrogen Bonds in $\text{Mn}[\text{OC}(\text{NH}_2)_2]_6(\text{ClO}_4)_3$

bond D-H...A	position of A	dist, Å			angle, deg D-H-A
		D-H	H...A	D...A	
N(1)-H(1)...O(2)	$2/3 - x, 1/3 - y, 1/3 - z$	0.89	2.406 (8)	3.104 (12)	135.9 (7)
N(1)-H(2)...O(3)	$1/3 + y, 2/3 + x - 1, 1/6 - z$	0.70	2.789 (21)	3.358 (24)	139.9 (10)
N(2)-H(3)...O(1)	$y - x, -x, z$	0.87	2.158 (7)	2.940 (13)	149.1 (7)
N(2)-H(4)...O(2)	$1/3 - y, 2/3 + x - y, 2/3 + z$	0.77	2.682 (10)	3.360 (16)	147.4 (8)

distances and angles given in Tables III and IV. Tables of the thermal parameters for the non-hydrogen atoms, the hydrogen atom parameters and distances, and the observed and calculated structure amplitudes are available.³⁹

Results and Discussion

Hexakis(urea)manganese(III) perchlorate is isomorphous with the corresponding titanium(III)³⁴ and aluminum(III)³⁷ salts. The crystal consists of the $\text{Mn}(\text{urea})_6^{3+}$ cation (site symmetry $\bar{3}$) illustrated in Figure 1 and the ClO_4^- anions (site symmetry 2) joined by weak hydrogen bonds (see Table V). The large deviations of the N-H...O angles from 180° and the long H...O and N...O distances are characteristic of weak hydrogen bonds.

The most remarkable feature of the structure is the $\bar{3}$ symmetry of the cation, which requires all six Mn-O bonds to be equivalent, an apparent violation of the Jahn-Teller theorem. To our knowledge, there are no other reported structural data on a high-spin Mn(III) complex with six identical monodentate ligands although a number of tris(bidentate) complexes are known. The Mn-O distance of 1.986 (7) Å found in the hexakis(urea) complex is comparable to the average Mn-O distances observed in tris(2,4-pentanedionato)manganese(III) [1.981 (32) Å in the β form²⁶ and 1.993 (91) Å in the γ form³⁰] and in tris(tropolonato)manganese(III) [2.004 (97) and 1.995 (49) Å²⁵]. However, there is some question as to the validity of averaging Mn-O distances in distorted molecules where the range can be from 1.931 to 2.020 Å.²⁶ Certainly the Mn-O distance observed in this study is not unreasonable relative to other Mn-O bond lengths. The important question is why the Mn-O bonds are equivalent in an apparent violation of the Jahn-Teller theorem.

Before we discuss the Mn-O bond length in more detail, let us focus on the urea molecule to see if there are any unusual features in the ligand. There are a large number of urea-metal ion complexes reported, but we will consider only the isomorphous Ti(III) and Al(III) complexes and the Ti(urea)₆³⁺, 3I⁻³³ and the Cr(urea)₆³⁺, 3Cl⁻·3H₂O structures,⁴⁰ which all crystallize in a hexagonal space group. In these four structures the average distances in the coordinated urea molecule are C-O of 1.283 (16) Å and C-N of 1.325 (27) and 1.316 (18) Å. The free urea molecule in the solid state⁴¹ has dimensions of C-O = 1.270 (7) and C-N = 1.326 (6) Å, which are not significantly different from those in the coordinated molecule. The dimensions in our manganese complex shown in Figure 2 are C-O = 1.283 (15), C-N = 1.320 (16), and C-N = 1.305 (14) Å, which are indistinguishable from the average values in the four complexes or in the free urea. Therefore, we conclude that the urea molecule has no unusual features that could account for the six equivalent Mn-O bonds.

The most reasonable explanation for the equivalence of the Mn-O bond lengths is in terms of the "dynamic" Jahn-Teller effect. The differences in the mean-square displacements given in Table VI for the three isomorphous M(urea)₆³⁺ complexes are in agreement with the "dynamic" Jahn-Teller effect. The mean-square displacements for the metal ions are very similar in magnitude and orientation relative to the M-O bond. If

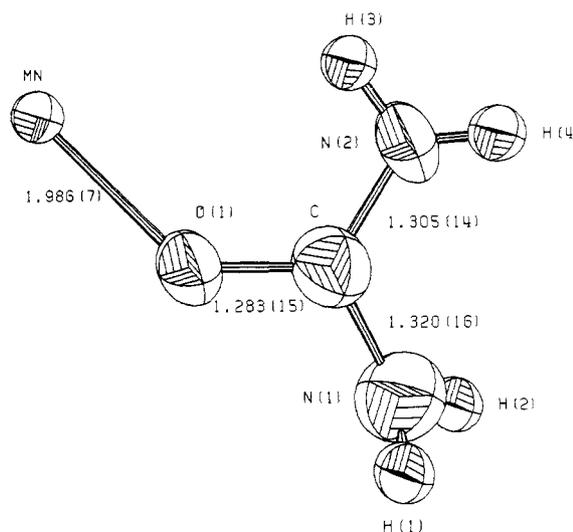


Figure 2. ORTEP view of the coordinated urea molecule in the $[\text{Mn}(\text{urea})_6]^{3+}$ cation showing the atomic number and thermal ellipsoids (50% probability level) and bond distances (Å) with estimated standard deviations in parentheses.

Table VI. $\text{M}[\text{OC}(\text{NH}_2)_2]_6(\text{ClO}_4)_3$ Mean-Square Displacements (M = Mn, Ti, Al)^a

	MSQ1	angle	MSQ2	angle	MSQ3	angle
Mn	0.155	133.6	0.155	116.7	0.204	55.4
O(1)	0.209	137.1	0.179	117.0	0.294	59.5
Ti	0.146	133.4	0.146	115.8	0.153	54.4
O(1)	0.156	144.2	0.194	125.5	0.240	94.2
Al	0.148	134.1	0.148	116.0	0.224	55.4
O(1)	0.158	155.4	0.188	104.8	0.246	70.9

^a MSQ_n is the *n*th mean-square displacement (Å) for the appropriate atom. Angle (deg) is the angle that the MSQ_n makes with the M-O bond.

there were major errors in the intensity data, we might have expected greater discrepancies in the thermal parameters and the mean-square displacements. In contrast only the mean-square displacements for the oxygen atom in the Mn complex are much larger in the direction of the bond. These differences in the mean-square displacements are in agreement with the predictions for a dynamic Jahn-Teller distorted molecule.

An extensive analysis of the dynamic Jahn-Teller in Cu(II) complexes has been reported,⁴² and we will use the same notation. Since there are no examples of a statically distorted hexakis(urea)manganese(III) cation, we can only compare our results with those for various tris(ligand)manganese(III) complexes. The average Mn-O bond distances in the five tris(ligand) molecules are essentially identical (vide supra), in spite of a large spread in the individual values. However, the Jahn-Teller radii, R_{JT} , calculated from the observed Mn-O distances vary markedly. The values of R_{JT} are 0.203 Å for the γ -tris(acetylacetonato), 0.072 Å for the β -tris(acetylacetonato), 0.171 Å for the tris(oxalato), and 0.217 and 0.110

(39) See paragraph at end of paper regarding supplementary material.

(40) Niven, M. L.; Nassimbeni, L. R. *Cryst. Struct. Commun.* **1980**, *9*, 1133.

(41) Caron, A.; Donohue, J. *Acta Crystallogr., Sect. B* **1969**, *B25*, 404.

(42) Ammeter, J. H.; Bürgi, H. B.; Gamp, E.; Meyer-Sandrin, V.; Jensen, W. P. *Inorg. Chem.* **1979**, *18*, 733.

Å for the two crystallographically independent tris(tropolonato) complexes.⁴³ In comparison the values of R_{JT} for 12 different Cu(II) complexes range from 0.252 to 0.355 Å.⁴²

The value of R_{JT} for the hexakis(urea)manganese(III) cation can be estimated from the difference in the mean-square displacement among the Mn(III), Ti(III), and Al(III) complexes. A value of 0.306 Å was calculated from $\Delta U(\text{Mn-O}) - \Delta U(\text{Ti-O})$. In the Al(III) complex $U(\text{O}) - U(\text{Al})$ was negative, which was somewhat surprising. However, the large size of the Al(III) crystal ($0.3 \times 0.4 \times 0.55$ mm), coupled with the use of Cu $K\alpha$ radiation and the lack of absorption corrections, could account for the negative value. Surprisingly, using the absolute value of $U(\text{O}) - U(\text{Al})$ gives a value of R_{JT} for Mn(III) of 0.355 Å. The two values of R_{JT} for Mn(III) calculated from the Ti(III) and Al(III) data are in reasonable agreement with the Cu(II) values but are significantly larger than the values calculated from the observed bond distances in the various tris complexes. Whether the large variation in R_{JT} for Mn(III) complexes vs. Cu(II) complexes is a consequence of a d^4 system compared to a d^9 case, or reflects the quality of the intensity data, or is related to the more reactive nature of Mn(III) complexes compared to those of Cu(II) can only be decided as additional data become available.

Additional support for a dynamic Jahn-Teller distortion is also found in the electronic spectral properties of the hexakis(urea) complex. The room-temperature visible absorption spectra of this complex (both the mull and the diffuse reflectance spectra) contain two very broad absorption envelopes centered at 8.70×10^3 and 19.10×10^3 cm^{-1} , respectively. But in the mull spectrum taken near liquid-nitrogen temperature, the 19.10×10^3 cm^{-1} absorption was resolved into two broad, overlapping bands, one maximum lying at 16.70×10^3 cm^{-1} and the other at 20.00×10^3 cm^{-1} .³² The lowest energy absorption was assigned as ${}^5B_{1g} \rightarrow {}^5A_{1g}$ (the components of the split octahedral 5E_g ground term), and the 16.70×10^3 cm^{-1} absorption as ${}^5B_{1g} \rightarrow {}^5E_g$. These assignments, in accord with those made by Fackler et al.,⁴ assume a tetragonally elongated manganese(III) complex during the time of the electronic transition. The ordering of term energies implicit in these assignments leads to a Dq value of 1.67×10^3 cm^{-1} , a Ds value of 1.71×10^3 cm^{-1} , and a Dt value of -0.372×10^3 cm^{-1} .⁴⁴

These parameters are similar to those obtained for manganese(III) complexes shown to be statically distorted.⁴ Furthermore, no other assignment of absorptions or ordering of terms proposed to account for the spectral properties of manganese(III) complexes leads to such close agreement of the Dq values reported for the isomorphous hexakis(urea) complexes of Ti(III),⁴⁵ V(III),⁴⁶ and Cr(III)⁴⁷ (1.67 – 1.70) $\times 10^3$ cm^{-1}). With the stabilization of the tetragonal structure over that of the reference, undistorted octahedral structure taken to be $Dt - 2Ds$, the apparent Jahn-Teller stabilization (E_{JT}) is -3.05×10^3 cm^{-1} , similar to those values reported both for manganese(III)⁴ and for copper(II)⁴² complexes.

An alternative means of estimating the stabilization energy of the distorted complex has been suggested provided $E_{JT} \gg h\nu > kT$ (where ν is the frequency of the Mn-O vibrational mode of e symmetry),⁴² namely, $4E_{JT} \simeq E({}^5B_{1g} \rightarrow {}^5A_{1g})$ or $E_{JT} \simeq 2.20 \times 10^3$ cm^{-1} . This estimated stabilization energy is similar to that calculated by the application of simple perturbation treatment; but the extension of the treatment leads to unacceptable values of the crystal field splitting parameter.

We conclude that $[\text{Mn(urea)}_6](\text{ClO}_4)_3$ is an example of the dynamic Jahn-Teller effect in a high-spin Mn(III) complex. The Mn(urea)_6^{3+} cation is required by the space group symmetry to have six equivalent Mn-O bonds. However, the mean-square displacement of the oxygen atom is much larger in the direction of the Mn-O bond compared to those in the isomorphous Ti(III) and Al(III) hexakis(urea) complexes, and the visible absorption spectrum can be interpreted in terms of a tetragonally distorted cation. The above three observations are typical of dynamically distorted Cu(II) complexes and, by extrapolation, high-spin Mn(III) complexes.

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Supplementary Material Available: Tables of the refined thermal parameters, the hydrogen atom positions, and observed and calculated structure amplitudes (6 pages). Ordering information is given on any current masthead page.

(43) The values of $R_{JT}^2 = \sum_{i=1}^6 \Delta d_i^2$ were calculated from the values of the Mn-O distances given in the pertinent reference.

(44) Ballhausen, C. J. "Introduction to Ligand Field Theory"; McGraw-Hill: New York, 1962; pp 101-102.

(45) Dingle, R. *J. Chem. Phys.* **1969**, *50*, 545.

(46) Dingle, R.; McCarthy, P. J.; Ballhausen, C. J. *J. Chem. Phys.* **1969**, *50*, 1957.

(47) Dingle, R. *J. Chem. Phys.* **1969**, *50*, 1952.