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Medium Ring Complexes. Square-Planar Complexes of Nickel(II) and Copper(II) with 1,5-Diazacyclooctane

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Extremely stable square-planar complexes of Ni(II) and Cu(II) with 1,5-diazacyclooctane (daco), a secondary, medium ring diamine, are described. The stability constants for the yellow nickel complex are much higher than for bis complexes of ethylenediamine and its derivatives. Although the stability constant for the copper complex is slightly lower than those for ethylenediamine complexes, the absorption maximum in the visible spectrum of the copper complex is observed at much higher energy and intensity than those for ethylenediamine complexes. Since the geometry of this chelate structure encompasses many of the factors which enhance the stability of square-planar complexes, this amine may be a prototype for square-planar complexes of first-row transition metals.

Introduction

A comparison of the formation constants of acyclic diamine complexes of Ni(II) and Cu(II) indicates that ethylenediamine (en) and its N- and C-substituted derivatives[1–4] are more stable than 1,3-diaminopropane (tn) and higher homologs.[5–6] Although N-alkylation of ethylenediamines might have been expected to cause increased complex stability due to an increased basicity, it was found that steric effects caused decreased stability.[1,2,4] Surprisingly, C alkylation of ethylenediamine caused increased complex stability even though the basicity of the amine was not significantly changed.[3] This effect was attributed to a shielding of the metal ion–nitrogen bonds from the polar solvent by the C substituents, thereby enhancing electrostatic interactions between the metal ion and nitrogen dipoles.[7]

A composite of effects leading to enhanced stability might be expected if, in the chelated structure, the metal ion formed part of a bicyclic ring rather than a monocyclic ring upon coordination with a secondary amine. The cyclic analogs of en, piperazine and its derivatives, form chelated bicyclic complexes with palladium and iridium[8] but form polymeric complexes with copper,[8] mercury, and cadmium.[9] The strain involved in compressing the bond angles of the piperazine ring to form chelates with the smaller transition metals was invoked[8] to account for this behavior. Homopiperazine (1,4-diazacycloheptane) is reported to form a bis complex with copper, but this complex was not isolated and had a lower stability constant than the bis-en complex.[10] Assuming that the strain would be minimized if an eight-membered cyclic diamine was used as the ligand, 1,5-diazacyclooctane (daco), the cyclic analog of tn, was chosen for study. Since daco is a secondary amine capable of forming highly symmetrical bicyclic rings when coordinated to a metal ion, very stable chelate structures were anticipated. In order to demonstrate the enhanced stability of this ligand with Ni(II) and Cu(II), the formation constants and magnetic properties of these complexes were obtained and the visible and infrared spectra were examined. On the basis of these measurements, we have found that daco forms extremely stable square-planar complexes with both Ni(II) and Cu(II). For example, the over-all stability constant for $[Ni(daco)_2]^{2+}$ is similar to that for $[Ni(EDTA)]^{2-}$.[11]

Experimental Section

Materials—Nickel(II) perchlorate hexahydrate and copper(II) perchlorate hexahydrate were obtained from the G. F. Smith Chemical Co. and were used without further purification.

1,5-Diazacyclooctane was prepared according to the procedure given by Buhle, Moore, and Wiseloge.[12a] The product was isolated and purified as the dihydrobromide salt.[12b]

Anal. Calcd for $C_6H_{16}N_2Br_2$: C, 26.20; H, 5.80; N, 9.80; Br, 57.90. Found: C, 26.56; H, 5.99; N, 9.65; Br, 57.9.

The solvents used for spectral analysis were Spectroquality grade obtained from Matheson Coleman and Bell.

Standard Solutions.—The standard solution of 1,5-diazacyclooctane was obtained by dissolving the purified dihydrobromide salt in a minimum amount of water and treating the solution with excess solid potassium hydroxide under a nitrogen atmosphere. The diamine was removed from the aqueous solution by extraction with purified diethyl ether. The ether solution was treated with distilled water, and the ether was removed by careful warming. The concentration of the base was determined by potentiometric titration with standard perchloric acid, and this solution was used for the determination of the formation constants.

Solutions of Cu (II) and Ni (II) were prepared by dissolving the hydrated perchlorate salts in distilled water. The resulting molarity (±2 ppt) of the aqueous solution of the metal salts was determined by electrodeposition.

Titration.—The reaction vessel consisted of a water-jacketed

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(1) F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **74**, 5243 (1952).

(2) F. Basolo and R. K. Murmann, *ibid.*, **76**, 211 (1954).

(3) F. Basolo, Y. T. Chen, and R. K. Murmann, *ibid.*, **76**, 956 (1954).

(4) H. Irving and J. M. M. Griffiths, *J. Chem. Soc.*, 213 (1954).

(5) G. B. Hares, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **78**, 1816 (1956).

(6) To be consistent with earlier workers the following abbreviations are used for the ligands: en = ethylenediamine, tn = 1,3-diaminopropane, N,N,-DiMeen = N,N′-dimethylethylenediamine, C,C′-TetraMeen = 2,3-diamino-2,3-dimethylbutane, daco = 1,5-diazacyclooctane, EDTA = ethylenediaminetetraacetic acid, *meso*-stien = *meso*-stilbenediamine, cyclam = 1,4,8,11-tetraazacyclotetradecane.

(7) D. L. Leussing, *Inorg. Chem.*, **2**, 77 (1963).

(8) F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 2772 (1958).

(9) P. J. Hendra and D. B. Powell, *ibid.*, 5105 (1960).

(10) J. M. Pagano, D. E. Goldberg, and W. C. Fernelius, *J. Phys. Chem.*, **65**, 1062 (1961).

(11) R. K. Murmann, *Inorg. Chem.*, **2**, 116 (1963).

(12) (a) E. L. Buhle, A. M. Moore, and F. G. Wiseloge, *J. Am. Chem. Soc.*, **65**, 29 (1943); (b) J. H. Billman and L. C. Dorman, *J. Org. Chem.*, **27**, 2419 (1962).

TABLE I

ACID DISSOCIATION CONSTANTS AND FORMATION CONSTANTS OF Cu(II) AND Ni(II) WITH DIAMINES

	en	tn	C,C'-TetraMeen	daco[d]		
Temp	25°	25°	25°	25°	35°	10°
$pK_{AH_2^{2+}}$	7.47[a]	8.89[c]	6.56[b]	7.25 ± 0.01	6.94 ± 0.01	7.68 ± 0.01
pK_{AH^+}	10.18	10.67	10.13	10.74 ± 0.01	9.96 ± 0.01	11.12 ± 0.03
Copper(II)						
Log K_1	10.76	9.77	11.63	10.56 ± 0.01	10.35 ± 0.06	10.93 ± 0.04
Log K_2	9.37	7.17	10.24	7.28 ± 0.03	6.58 ± 0.08	7.91 ± 0.04
Log K_T	20.13	16.94	21.87	17.84 ± 0.02	16.93 ± 0.07	18.84 ± 0.04
Nickel(II)						
Log K_1	7.60[a]	6.39[c]	...	...	...	...
Log K_2	6.48	4.39	...	...	...	...
Log K_3	5.03	(1.23)				
Log K_T	19.11	12.01	14.68	18.68 ± 0.12[e]	17.55 ± 0.11	19.48 ± 0.01

[a] Ref 2. [b] Ref 3. [c] R. Näsänen, M. Koskinen, R. Salonen, and A. Kiiski, *Suomen Kemistilehti*, **38B,** (4) 81 (1965). [d] The actual temperatures of measurement were 25, 36.1, and 10.5°. [e] Values of log K_1 and log K_2 were obtained from pH measurements.

TABLE II

ANALYTICAL DATA OF 1,5-DIAZACYCLOOCTANE COMPLEXES

Complex	Color	Mp, °C	μ_{eff}, BM 25°	% C[a]		% H[a]		% N[a]	
				Calcd	Found	Calcd	Found	Calcd	Found
$[Cu(daco)_2](ClO_4)_2$	Maroon	208	1.88	29.35	29.2	5.71	5.8	11.42	11.20
$[Ni(daco)_2](ClO_4)_2$	Yellow	266	0.62[b]	29.60	29.90	5.76	6.10	11.53	11.10
$[Ni(daco)_2(H_2O)_2](ClO_4)_2$	Yellow	...	...	27.59	27.48	6.13	6.13	10.73	10.73

[a] The microanalyses were performed by the Microanalytical Laboratory, Chemistry Department, University of California, Berkeley, Calif. [b] This residual paramagnetism is much lower than the usual value near 3.2 BM for the fully paramagnetic ion: B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 6, 198 (1964).

cell which was maintained at 10.5, 25.0, and 36.1 ± 0.1° by recirculating water from a constant temperature bath through the outer jacket.[13] A 10-ml buret capable of reading 0.02 ml was used for the freshly prepared amine solution, and the entire apparatus was kept under an atmosphere of presaturated nitrogen throughout the titration. A magnetic stirrer was provided to ensure proper mixing. A saturated calomel electrode and a glass electrode were used in conjunction with a Beckman Expandomatic pH meter. The expanded scale was used and the meter was standardized with precision Beckman buffer solutions and calibrated before and after each titration. All measurements were made in 0.50 M KNO_3 to ensure constant ionic strength and to correlate these results with those of Basolo and Murmann.[1-3] At least two titrations were carried out for each complex at 25°.

Determination of Formation Constants.—The stepwise formation constants were determined by the familiar Bjerrum titration technique,[14] modified by Verhoek[15] and extended by Basolo and Murmann.[1-3]

The formation constants were obtained from plots of $\bar{n}$ *vs.* p[A]. The values of p[A] near $\bar{n} = 0.5$ and 1.5 were used to determine log K_1 and log K_2, respectively, based on the assumption that the species MA_2 is of negligible concentration at $\bar{n} = 0.5$ and that M^{2+} is negligible at $\bar{n} = 1.5$.[16] These values were obtained at three different temperatures.[17] The formation curve was extremely reproducible at room temperature and above but the values drifted during the titration at 10° due to the longer time required for the attainment of equilibrium after each addition.

The ΔH values (estimated error 5%) were calculated from the slopes of the best straight lines obtained from plotting log K_T *vs.* $1/T$ at three different temperatures. Other thermodynamic quantities were calculated in the usual way.

A tabulation of acid dissociation constants for selected diamines and their formation constants with Ni(II) and Cu(II) is presented in Table I.

General Preparation of Solid Complexes.—A sample of 3.66 g (0.01 M) of nickel(II) perchlorate hexahydrate or 3.71 g (0.01 M) of copper(II) perchlorate hexahydrate was dissolved in 10–15 ml of anhydrous ethyl alcohol. This solution of nickel(II) perchlorate or copper(II) perchlorate was then added dropwise to an excess of daco dissolved in diethyl ether with constant stirring. The precipitated complex was isolated by filtration, washed with anhydrous ether, recrystallized from ethanol or water, and dried in a desiccator. Further drying was accomplished by warming under vacuum. The yield of product ranged from 75 to 85%.

The hydrated complex was prepared by mixing aqueous solutions containing 2:1 stoichiometric quantities of the amine and the metal perchlorate. The solvent was removed by means of a rotary evaporator to give crystalline complexes. The anhydrous salt could be prepared by careful heating at 110° in a high-vacuum line for 24 hr. The analytical data for these complexes are tabulated in Table II.

Spectral Measurements.—The infrared absorption spectra of the solid complexes (KBr and Nujol) were obtained using a Beckman IR-8 infrared spectrophotometer. The visible absorption spectra of the complexes in several solvents were obtained with a Cary Model 14 recording spectrophotometer using matched 1-cm quartz cells. The visible spectral data are collected in Table III.

Magnetic Susceptibility Measurements.—The magnetic moments of the solid complexes were determined by the Gouy method at room temperature. A double-ended Gouy tube was calibrated using $Hg[Co(NCS)_4]$ as the standard, and the magnetic moments were calculated by using the procedure described by Figgis and Lewis.[18]

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(13) H. Freiser, R. G. Charles, and W. D. Johnston, *J. Am. Chem. Soc.*, **74**, 1383 (1952).

(14) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(15) G. A. Carlson, J. P. McReynolds, and F. H. Verhoek, *J. Am. Chem. Soc.*, **67**, 1334 (1945).

(16) T. J. Lane, A. J. Kandathial, and S. M. Rosalie, *Inorg. Chem.*, **3**, 487 (1964).

(17) An appendix containing the original data and the FORTRAN program used for the calculation of the formation constants has been deposited as Document No. 8910 with the ADI Auxiliary Publications Project, Photoduplication service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $2.50 for photoprints or $1.75 for 35-mm microfilm. Advanced payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(18) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishing Co., Inc., New York, N. Y., 1960, p 412.

TABLE III

VISIBLE ABSORPTION SPECTRAL DATA FOR SQUARE-PLANAR COMPLEXES OF NICKEL(II) AND COPPER(II) WITH DIAMINES

	Solvent	λ_{max}, cm^{-1}	ϵ_{max}	Ref
2:1 Complexes				
$[Ni(C,C'\text{-TetraMeen})_2](NO_3)_2$	Water	23,050	63.8	3
$[Ni(\textit{meso}\text{-stien})_2]Cl_2$	95% CH_3CH_2OH	23,450	66	*d*
$[Ni(daco)_2](ClO_4)_2$	Water	22,500	115	*a*
	CH_3NO_2	22,450	112	*a*
	CH_3CN	22,450	120	*a*
$[Cu(en)_2]SO_4$	Water	18,200^b	63	4
$[Cu(C,C'\text{-TetraMeen})_2](NO_3)_2$	Water	18,300	120	*c*
$[Cu(daco)_2](ClO_4)_2$	Water	19,950	295	*a*
	CH_3NO_2	20,250	337	*a*
	CH_3CN	19,800	304	*a*
1:1 Complexes				
$[Cu(en)]SO_4$	Water	15,400^b	37.5	4
$[Cu(daco)](ClO_4)_2$	Water	15,700	116	*a*

[a] This work. [b] Estimated. [c] R. G. Wilkens, *J. Chem. Soc.*, 4521 (1957). [d] W. C. E. Higginson, S. C. Nyburg, and J. S. Wood, *Inorg. Chem.*, **3**, 463 (1964).

Results and Discussion

The Nickel Complex.—As evidenced by the high formation constant (Table I), bis-daco complexes of Ni(II) are far more stable than all other diamine complexes in the absence of π bonding. However, steric interaction between ligands is minimized relative to normal secondary amines as the alkyl substituents are pinned back by the ring structure. Thus, the enhanced basicity of the secondary amine is not reduced by intramolecular steric interactions and the maximum inductive effect is felt. This fact coupled with the shielding of the central metal ion from solvation by the hydrocarbon chain[7] could account for this stability. That a square-planar complex of Ni(II) is formed is confirmed[19] by its diamagnetic behavior and its visible absorption spectrum, which shows only a single transition. This absorption band is reported[20] to correspond to a transition from $^1A_{1g}$ to $^1A_{2g}$ in a d^8 system of D_{4h} symmetry. As shown in Table III, the position of the absorption maximum is similar to that observed in $[Ni(C,C'\text{-TetraMeen})_2]^{2+}$, $[Ni(\textit{meso}\text{-stien})_2]^{2+}$, and $[Ni(cyclam)]^{2+}$, where square-planar geometry has been demonstrated.[3,21] The similarity of $[Ni(daco)_2]^{2+}$ and $[Ni(C,C'\text{-TetraMeen})_2]^{2+}$ is further substantiated by the observation that no 1:1 complex of the diamine and Ni(II) is formed.[3] The visible spectra of solutions of 1:1 stoichiometry show that the position of the maximum is identical with and the absorbance is one-half that of solutions of 2:1 stoichiometry. If excess diamine is added, the position of the maximum and the absorbance are unchanged.

By the use of molecular models, the most favorable conformation of the square-planar bis-daco complexes can be envisioned with both eight-membered rings in the chair–boat form (Figure 1). In this configuration octahedral coordination would be prevented since the axial positions of the ion are relatively shielded from solvation. This type of shielding was invoked by Higginson, Nyburg, and Wood[21a] to explain the *meso*-stilbenediamine and the *d,l*-stilbenediamine complexes of nickel.

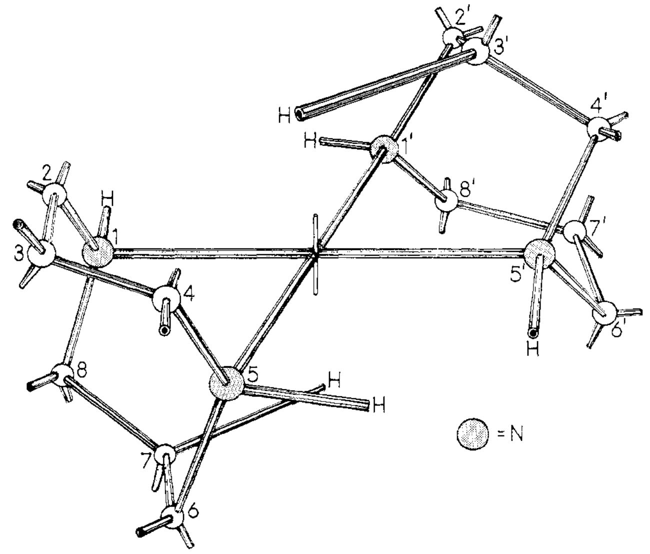

Figure 1.—Idealized conformation of square-planar 1,5-diazacyclooctane complexes of Ni(II) and Cu(II).

This complex is rather resistant to attack by external reagents. Decomposition is not observed at room temperature in water and alcohol or on solution in 12 *N* HCl, and only slow discoloration is apparent in excess EDTA. However, the addition of cyanide discharges the color immediately. This behavior is similar to that of the nickel complex of cyclam as described by Bosnich, Tobe, and Webb.[21b]

When the bis-daco complex was prepared in water, the analysis corresponded to $[Ni(daco)_2(H_2O)_2](ClO_4)_2$; however, the water was easily removed by careful warming under vacuum. The infrared spectra of the hydrated and anhydrous material were almost identical except for broad absorption in the 3500 cm^{-1} region, suggesting that the water is not bound to the metal

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(19) Bridging two metal atoms by daco rings to form a dinuclear complex or polymeric species is extremely unlikely. These complexes would contain numerous nonbonded interactions and would be very unstable.

(20) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958).

(21) (a) W. C. E. Higginson, S. C. Nyburg, and J. S. Wood, *Inorg. Chem.*, **3**, 463 (1964); (b) B. Bosnich, M. L. Tobe, and G. A. Webb, *ibid.*, **4**, 1109 (1965).

ion but is incorporated in the crystal lattice. No evidence for complex formation between the perchlorate ion and $[Ni(daco)_2]^{2+}$ was found on inspection of the infrared spectrum of the anhydrous salt as was observed for certain secondary amine complexes of nickel by Pavkovic and Meek.[22]

The Copper Complex.—The stepwise formation constants for the bis-daco complexes of Cu(II) are less than the corresponding values of en and its N- and C-substituted derivatives, but greater than the values of tn. However, bis-daco complexes of Cu(II) have been isolated in contrast to the behavior of piperazine where the precipitation of copper hydroxide is observed.[10]

The deep maroon color of $[Cu(daco)_2]^{2+}$ was somewhat surprising and the position of the absorption maximum in the visible spectrum was found to be much higher in energy than those of en complexes (Figure 2). In fact, the energy is about 1700 cm^{-1} higher and the molar extinction coefficient is over twice as high as those for any $[Cu(diamine)_2]^{2+}$ reported (Table III). This spectral data would indicate that the tetragonal distortion is extremely high and that inductive effects greatly predominate over steric effects in this complex.[23] Perhaps the intensification of the d–d transition can be attributed to vibronic interactions[24] and to the formation of strong covalent bonds between the ligand and the metal ion.

For Cu(II) and Ni(II) diamine complexes it has been observed that,[25–27] in general, as the formation constants increase, the absorption maximum is shifted to higher energies. The behavior of $[Cu(daco)_2]^{2+}$ reveals a situation where the formation constant is lower than those for en complexes but the position of the absorption maximum appears at higher energy. The ratio $(\sigma_{Cu}/\sigma_{Ni})$ between the wavenumbers of the absorption maxima for the Cu(II) and Ni(II) daco complexes is only 1.1, whereas this ratio is usually in the range from 1.6 to 1.8 for highly tetragonal complexes.[28] Even the visible absorption spectrum of the 1:1 complex of daco with Cu(II) exhibits a maximum at higher energy than other diamine complexes, which again could be attributed to the greater inductive effect of the amine. It is interesting to note that $[Cu(en)]^{2+}$ also forms purple to red intermediate complexes with cyanide,[25] indicating high tetragonality in these species. The observed magnetic moment of 1.88 BM for the copper–daco complexes is slightly greater than that for copper–en complexes (1.85 BM).[27]

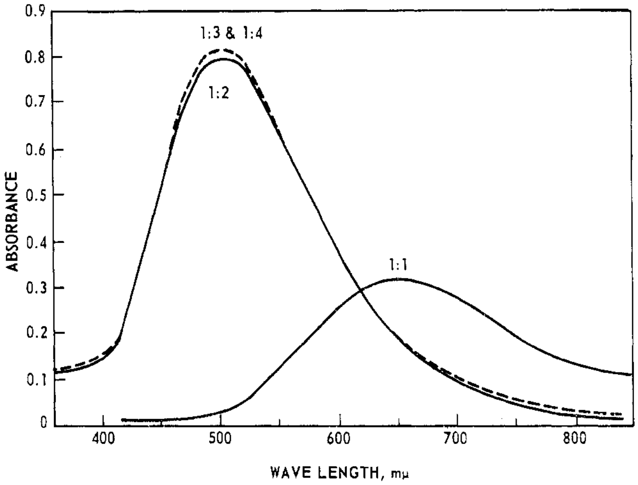

Figure 2.—The visible absorption spectrum of Cu(II) 1,5-diazacyclooctane complexes. The molar ratio $[Cu^{2+}]$: [ligand is shown.

No thermochromism was observed when the perchlorate salts were heated, and the compounds showed no signs of decomposition during the heating process.

In order to obtain an estimate of the magnitude of the thermodynamic constants, ΔH was determined by carrying out additional potentiometric titrations at 10 and 36.1° and ΔS was calculated at 25°. The over-all enthalpy change (kcal mole^{-1}) on complexation was found to be -27.5 for $[Cu(daco)_2]^{2+}$ and -26 for $[Ni(daco)_2]^{2+}$, and the entropy change (cal mole^{-1} K^{-1}) was -11 and -2 for the Cu(II) and Ni(II) complexes, respectively. Although correlation of data between different investigators using different analytical procedures is difficult,[29,30] we feel that the magnitude of the enthalpy change observed by potentiometric titration is consistent with the other data which we have collected. As expected, the enthalpy changes are more negative than those reported[1–4] for ethylenediamine derivatives. The magnitude of the entropy change, which is obtained as a small difference between two large numbers, is not as reliable and cannot be attributed to any specific effects.

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(22) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 1091 (1965).

(23) D. W. Meek and S. A. Ehrhardt, *ibid.*, **4**, 584 (1965).

(24) C. J. Ballhausen, *Progr. Inorg. Chem.*, **2**, 251 (1960).

(25) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 887 (1956).

(26) I. Poulson and J. Bjerrum, *ibid.*, **9**, 1407 (1955).

(27) C. D. Russell, G. R. Cooper, and W. G. Vosburgh, *J. Am. Chem. Soc.*, **65**, 1301 (1943).

(28) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 124.

(29) G. H. McIntyre, Jr., B. P. Block, and W. C. Fernelius, *J. Am. Chem. Soc.*, **81**, 529 (1959).

(30) F. J. C. Rossotti, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishing Co., Inc., New York, N. Y., 1960 p 37.