

ETHYLENEDIAMINE ADDITION COMPOUNDS OF METAL PERCHLORATES

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Abstract—The ethylenediamine addition compounds of the perchlorates of lithium, magnesium, calcium, strontium, barium, copper and zinc were prepared by the direct union of ethylenediamine and the corresponding metal perchlorate. The thermal stabilities of these compounds were studied by differential thermal analysis and thermogravimetric analysis methods.

THE anhydrous perchlorates of the alkaline earth metals are excellent absorbents for water and for ammonia. In this work there is reported additional compounds of alkaline earth perchlorates with ethylenediamine (en).

The addition compounds of the alkaline earth perchlorates and ammonia have already been studied⁽¹⁾ and their composition shown to vary with the conditions of temperature and pressure owing to the relatively high vapour-pressure of the ammonia over the compounds. Because of the lower volatility of ethylenediamine and because of the formation of chelate rings, addition compounds of it and the alkaline earth perchlorates might be expected to be more stable than the corresponding ammonia compounds.

The combination in a single molecule of a combustible, organic component, a potentially powerful oxidant, and a flame colouring agent should give to such compounds some startling properties.

EXPERIMENTAL

Reagents. The alkaline earth perchlorates used were reagent grade chemicals obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio. Anhydrous ethylenediamine was purified by distillation. The copper and zinc perchlorate hexahydrates were prepared by treating an excess of the corresponding carbonate with 70 per cent perchloric acid, filtering, crystallizing, filtering and finally recrystallizing from water.

Preparation. In general the ethylenediamine derivatives were prepared by the careful addition of the anhydrous metal perchlorate to an excess of ethylenediamine with stirring. The reactions were exothermic and caution was taken to avoid spattering. It was not necessary to obtain complete dissolution. The mixture was cooled to room temperature and the precipitate washed by decantation with 1:10 ethanol-ethyl acetate to remove the excess ethylenediamine. The material was sucked dry and dried under reduced pressure over anhydrous magnesium perchlorate. Some necessary variations in individual cases are described in detail below.

LiClO₄·2en. Anhydrous lithium perchlorate was placed in a vacuum desiccator over ethylenediamine and permitted to absorb the vapour until the material became pasty. The product was washed twice with ethyl acetate. It was then dissolved in ethyl acetate by warming to 50°. The solution was filtered. On cooling a white crystalline compound precipitated which was filtered off, recrystallized from ethyl acetate again and dried under reduced pressure over anhydrous magnesium perchlorate.

In some preparations the initial absorption process was allowed to proceed until complete solution resulted; crystallization of the addition compound from the ethyl acetate could not then be achieved.

⁽¹⁾ G. F. SMITH and E. G. KOCH, *Z. Anorg. Chem.* **223**, 17 (1935).

Ethanol was avoided in the washing operation as early experience showed the addition compound could not be recovered.

$\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{en}$. This compound was prepared in the same manner as the lithium compound except that 1:10 ethanol-ethyl acetate was used as the wash solution. The general method of preparation failed to give a homogeneous product.

$\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{en}$; $\text{Sr}(\text{ClO}_4)_2 \cdot 4\text{en}$; $\text{Ba}(\text{ClO}_4)_2 \cdot 4\text{en}$; $\text{Cu}(\text{ClO}_4)_2 \cdot 2 \cdot 5\text{en}$; $\text{Zn}(\text{ClO}_4)_2 \cdot 3\text{en}$. These compounds were all prepared by the general method described above. The hexahydrates rather than the anhydrous perchlorates were used to prepare the zinc and copper compounds.

TABLE 1.—SUMMARY OF ANALYTICAL RESULTS
(en = ethylenediamine)

Compound	Metal		Perchlorate calcd.* (%)	Amine		Total (%)
	Theor. (%)	Exp. (%)		Theor. (%)	Exp. (%)	
$\text{LiClO}_4 \cdot 2\text{en}$	3.06	3.002	43.03	53.00	52.16	98.19
$\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{en}$	6.032	6.034	49.38	44.64	44.17	99.75
$\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{en}$	8.35	8.38	41.60	50.11	49.98	99.96
$\text{Sr}(\text{ClO}_4)_2 \cdot 4\text{en}$	16.63	16.62	37.75	45.57	45.21	99.58
$\text{Sr}(\text{ClO}_4)_2 \cdot 2\text{en}$	21.55	21.61	49.06	29.51	28.83	99.50
$\text{Ba}(\text{ClO}_4)_2 \cdot 4\text{en}$	23.85	23.70	34.32	41.64	41.54	99.56
$\text{Cu}(\text{ClO}_4)_2 \cdot 2 \cdot 5\text{en}$	15.41	15.32	47.99	36.40	36.55	99.86
$\text{Zn}(\text{ClO}_4)_2 \cdot 3\text{en}$	14.71	14.76	44.94	40.50	40.48	100.18

* Calculated from the metal analysis.

$\text{Sr}(\text{ClO}_4)_2 \cdot 2\text{en}$. Strontium ethylenediamine perchlorate was heated at 165–170° in a stream of heated, dry air for 1 hr. The liquid so obtained solidified on cooling and could be cast into sticks of considerable physical strength.

Analysis. Ethylenediamine was determined by titration of a water solution of the compound with standard hydrochloric acid using methyl purple indicator. For the copper compound it was necessary to determine the end-point potentiometrically because of the colour of the copper amine. Owing to the insolubility of the magnesium compound, it was dissolved in an excess of standard hydrochloric acid and back titrated with standard alkali.

Magnesium, calcium, strontium, barium and zinc were determined by titration with EDTA using Eriochrome Black T as indicator. A small and known amount of magnesium was added to sharpen the end-point in the titrations of calcium, strontium and barium. Copper was determined by electro-deposition. Lithium was determined by passage of the aqueous solution of the sample through a column of IR-120, a strong cation exchange resin, in the hydrogen form and titration of the perchloric acid in the eluate with standard sodium hydroxide.

The analytical results are tabulated in Table 1.

Properties. The addition compounds were found to be remarkably hygroscopic, some gaining up to 66 per cent in weight of water in 24 hr on exposure to air saturated with moisture. The odour of ethylenediamine was noticed over the calcium, strontium and barium compounds only. All of the compounds proved readily soluble in water with the exception of the magnesium compound, the only alkaline earth compound which was not deliquescent; it was readily soluble in dilute acid.

All of the compounds were obtained white except for the copper compound which exhibited the characteristic, deep blue copper-ammine colour. There is some tendency for the white compounds to turn slightly yellow on standing although this varied from batch to batch and seemed to be a property of the ethylenediamine for compounds prepared from freshly distilled ethylenediamine were still white after four months.

All of the compounds burned with self-sustaining flames when ignited on a steel plate with a flame. They yielded the characteristic colours of the metal and considerable smoke. The vigour of this open-plate burning increased in the order calcium, zinc, magnesium, barium, strontium, lithium and copper. The copper compound burned with detonation of individual crystals.

Differential thermal analysis (DTA). All of the compounds prepared with the exception of the copper compound were subjected to a differential thermal analysis study. The DTA apparatus used was that described by GORDON and CAMPBELL,⁽²⁾ modified so that the temperature of the sample was obtained by a separate thermocouple; this resulted in greater stability by eliminating the interruption in the differential thermocouple circuit. The temperature of the sample was plotted directly on a Brown Electronic 3-channel, 50 mV full scale, point plotting recorder utilizing all three channels. The differential temperature was plotted on a Brown Electronic 12 mV full scale, strip chart recorder using a 28-gauge iron-constantan thermocouple. Sample temperature was related to the corresponding

TABLE 2.—DIFFERENTIAL THERMAL ANALYSIS OF ETHYLENEDIAMINE ADDITION COMPOUNDS

Compound	Endotherms (°C)	Exotherms (°C)	Decomposition (°C)
LiClO ₄ ·2en	95 (2)* 268 (4)	315	357
Mg(ClO ₄) ₂ ·3en	110 (3) 315 (6)	326 (88)	326
Ca(ClO ₄) ₂ ·4en	177 (12)	285 (45)	295
Sr(ClO ₄) ₂ ·4en	168 (55) 192 (11)	293	317
Ba(ClO ₄) ₂ ·4en	118 (1) 176 (2)	277	295
Zn(ClO ₄) ₂ ·3en	142 (4)	270 (47)	275

* The temperature in parenthesis is the temperature deviation from the apparent base line for the corresponding endotherm or exotherm. The absence of this value indicates the data was not available as the decomposition was accompanied by an explosion which terminated the run.

points on the differential temperature plot by utilizing the built-in microswitch of the point plotting recorder; each time a point was plotted on the sample temperature curve, the microswitch opened causing a slight kick in the differential temperature plot. Thermocouples were checked with standard melting point samples of tin and zinc and with boiling water. The temperature was increased linearly throughout the temperature range used and was accurate to within 2°, the recorded reading always being high.

The operation of the DTA apparatus was checked by a run on silver nitrate which GORDON and CAMPBELL reported as having marked deflexions in the expected range of the ethylenediamine addition compounds. Of the six temperatures at which deflexions were noted on the curve reported by GORDON and CAMPBELL, acceptable agreement was obtained at two and exact agreement at the other four.

Efforts were made to keep the size of the particles, the size of the sample, packing and positioning as uniform as possible. The hygroscopicity of the compounds required that the work be done quickly but even so the absorption of water did cause some shifting of the DTA base line. Calculations were made from the new or apparent base line. The results are summarized in Table 2.⁽³⁾

Thermogravimetric analysis. The thermobalance used was an equal-arm balance converted to positive displacement and direct reading by the variable transformer-electronic arrangement of GORDON and CAMPBELL.⁽⁴⁾ The temperature of the sample was recorded on a Brown Electronic 3-channel point plotting recorder. The output of the demodulator was fed into a Brown Electronic strip chart recorder. The temperature of the sample was manually transferred to the thermogravimetric curve as the analysis proceeded. The recorder was found to be linear throughout the 200 mg range used, the greatest source of error being the reading of the chart. Again, owing to the hygroscopicity of the materials being studied, some initial drift (gain in weight) was recorded and the actual weight of the sample was taken as that during the linear portion at 100° at which time the apparatus had equilibrated and no true weight loss had yet resulted.

The results are summarized in Table 3.⁽³⁾

⁽²⁾ S. GORDON and C. CAMPBELL, *Analyt. Chem.* **27**, 1102 (1955).

⁽³⁾ The actual DTA and TGA curves obtained will be found in the Master of Science Thesis of H. W. WHARTON, The Library, Iowa State University, Ames, Iowa, (1958).

⁽⁴⁾ S. GORDON and C. CAMPBELL, *Analyt. Chem.* **29**, 298 (1957).

RESULTS AND DISCUSSION

The composition of the addition compounds is about that expected: two molecules of ethylenediamine adding to the lithium salt, three to magnesium and zinc, and four to the alkaline earths. The figure of 2.5 for copper is interesting as further evidence of the great difficulty of forcing copper(II) to be hexavalent.

Most inorganic compounds undergo thermal decomposition with definite losses in weight at specific temperatures and exhibit wide temperature regions of stability. The metal ethylenediamine perchlorates, however, exhibit a gradual, nearly linear loss

TABLE 3.—THERMOGRAVIMETRIC ANALYSIS OF ETHYLENEDIAMINE ADDITION COMPOUNDS

Addition Product	Decomposition temperature (°C)	Equivalent mol. wt. loss (en = 60)	No. of en lost at decomposition
LiClO ₄ ·2en	308	61.0	1
Mg(ClO ₄) ₂ ·3en	327	60.5	1
Ca(ClO ₄) ₂ ·4en	288	122	2
Sr(ClO ₄) ₂ ·4en	323	200	3
Ba(ClO ₄) ₂ ·4en	305	188	3
Zn(ClO ₄) ₂ ·3en	258	29.6	0.5

in weight throughout the heating and the endotherms obtained in the DTA studies were unusually broad and rather poorly defined. Together these indicate that ethylenediamine is released gradually on heating until the final explosive decomposition temperature is reached. Primarily of course, this is a matter of the conditions of the experiment; were the rate of heating sufficiently slow and a constant atmosphere maintained above the compounds, equilibrium and definite composition could be obtained but this would defeat the very purpose and design of the DTA and thermogravimetric methods. That equilibrium and definite composition can be achieved is evident from the one study made in this direction, the preparation of the strontium diethylenediamine compound.

The decomposition temperatures obtained by the two methods for any one compound agree about as well as can be expected in view of the difference in rate of heating. For all of the compounds the decomposition temperatures fall in the range 258–357°. Ethylenediamine perchlorate decomposes violently in this same range,⁽⁵⁾ at 280°. The vigour of the final decomposition depends on the composition of the compound at that point. Those compounds bearing only one molecule of ethylenediamine as they reached the decomposition temperature explode: lithium, strontium and barium. The final decomposition of the zinc perchlorate, bearing 2.5 molecules of ethylenediamine at that point, is not explosive.

LiClO₄·2en. The DTA curve showed primarily the difference in thermal conductivity of the material and the inert reference material. A shift in the base line resulted from the increased thermal conductivity of the molten material, for this compound melted at about 75°. An endotherm at 270° corresponded to the loss of one ethylenediamine prior to decomposition, the loss in weight starting at 120° and continuing until the decomposition temperature. Both curves terminated at the decomposition temperature. The explosion at the decomposition temperature was the most violent

⁽⁵⁾ K. A. HOFFMAN, K. HOBOLD and F. QUOOS, *Liebigs Ann.* 396, 314 (1912).

of any of the compounds studied. Only one molecule of ethylenediamine was present at this point.

$\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{en}$. The DTA and thermogravimetric data indicated only the loss of one ethylenediamine at the decomposition temperature. The decomposition took place with the very rapid evolution of heat, white smoke and white flame; because no explosion occurred, it was possible to follow the DTA beyond the decomposition temperature. The light gray residue showed the presence of chloride and oxide.

$\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{en}$. The gradual and nearly linear loss of weight began at 125° corresponding to the endotherm beginning at about 140° . This corresponded to the abrupt loss of the first molecule of ethylenediamine, tailing off as the second was lost prior to decomposition. The correspondingly smaller exotherm at decomposition compared with that of the magnesium compound was confirmed by the less vigorous decomposition. Chloride and oxide were found in the brownish residue.

$\text{Sr}(\text{ClO}_4)_2 \cdot 4\text{en}$. The DTA curve for this compound was as spectacular as its final decomposition. The endotherm at 165° corresponded in part to the loss of two molecules of ethylenediamine as shown by the preparation of the diethylenediamine compound by uniform heating of this compound at $165\text{--}170^\circ\text{C}$ in a stream of heated, dry air. This endotherm tailed off to about 260° where the thermogravimetric data indicated that all of the second ethylenediamine had been released. The decomposition at 317° was a violent explosion with brilliant scarlet fire and smoke.

$\text{Ba}(\text{ClO}_4)_2 \cdot 4\text{en}$. Information from the two curves correlated well. Only one molecule of ethylenediamine remained at the decomposition temperature and the decomposition occurred with an explosion.

$\text{Zn}(\text{ClO}_4)_2 \cdot 3\text{en}$. Repeated runs on the DTA of this compound gave a large base line shift up to 200° . Corresponding to this there was no weight loss up to about 225° . The first loss in weight corresponded to one-half molecule of ethylenediamine. Thus 2.5 molecules remained at decomposition. The decomposition was vigorous but not explosive. Chloride ion and oxide were present in the carbonaceous residue.

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