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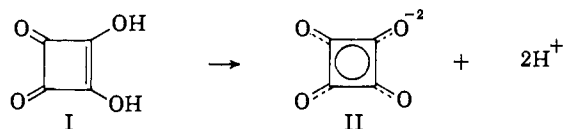
New Aromatic Anions. VII. Complexes of Squarate¹ Ion with Some Divalent and Trivalent Metals

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Complexes of squarate¹ ion (diketocyclobutenediol dianion, II) with divalent Cu, Fe, Zn, Ni, Mn, Co, Ca, and Mg, and with trivalent Al, Fe, and Cr, have been prepared and characterized. All of the divalent metal complexes are dihydrates, and all except the Cu and Ca compounds have the same structure. The three trivalent metal complexes are isostructural and have the general formula $MC_4O_4(OH)(H_2O)_2$. The magnetic moments of the divalent metal compounds indicate that they are high-spin complexes, but the Fe(III) and Cr(III) complexes show somewhat reduced paramagnetism. A polymeric structure is suggested for divalent metal complexes.

The compound diketocyclobutenediol (I) was first synthesized in 1959 by Cohen, Lacher, and Park³ and was shown by these workers to be a strong acid. Only the potassium salt of I has been reported to date. The present investigation of the transition metal derivatives



of squarate ion (II) was undertaken because it seemed likely that these complexes would have unusual structures. Also, in view of the postulated relationship⁴ between II and croconate ion, $C_5O_5^{2-}$, it was of interest to determine if metal derivatives of squarate ion would resemble those of croconate.⁵ Marked resemblances were indeed found between metal complexes of squarate and croconate ions. All of these compounds appear to be coordination polymers linked through oxygen. Like many other coordination polymers, these compounds are all highly crystalline substances. They char without melting when heated above 200°. Other similarities and differences in the compounds of the two series are noted below.

Divalent Metal Squarates.—The complexes of divalent Ca, Mn, Fe, Co, Ni, Cu, and Zn were all synthesized readily from aqueous solutions of appropriate salts of the cations and dipotassium squarate. All of the salts were shown by analysis to be dihydrates with the general formula $MC_4O_4 \cdot 2H_2O$, whereas the corresponding croconates are trihydrates. The squarate ion is colorless and the derivatives generally exhibit pale colors characteristic of the metal ions. Measurements of the static magnetic moment by the Gouy method showed that the divalent transition metal squarates, like the croconates, are all high-spin complexes (Table I).

The squarates of divalent Mn, Fe, Co, Ni, Mg, and Zn all have nearly identical X-ray powder patterns and so must have the same structure. Slight differences in lattice spacing are found as the radius of the metal ion changes. Typical data are given in Table II. It is striking that the divalent squarates, like the croconates,⁵ form an extensive isostructural series. The powder pattern of calcium squarate dihydrate is unique (Table II), probably reflecting a structural difference resulting from the relatively large radius (0.99 Å.) of the calcium ion. Copper(II) squarate also appears to have a unique

(1) The names "squaric acid" and "squarate" for diketocyclobutenediol and its dianion have come into use by workers in this field.³ For reasons of brevity and convenience, the term "squarate" will be used for the dianion II throughout this paper.

(2) J. D. Park, S. Cohen, and J. R. Lacher, *J. Am. Chem. Soc.*, **84**, 2919 (1962).

(3) S. Cohen, J. R. Lacher, and J. D. Park, *ibid.*, **81**, 3480 (1959).

(4) R. West, H. Y. Niu, D. L. Powell, and M. V. Evans, *ibid.*, **82**, 6204 (1960).

(5) R. West and H. Y. Niu, *ibid.*, **85**, 2586 (1963).

structure (Table II), although copper(II) croconate has the typical structure for the divalent croconate series.

TABLE I
MAGNETIC MOMENTS OF SQUARATE COMPLEXES

Squarate	Temp., °K.	μ , Bohr magnetons	ϵ^a
Cu(II)	295	1.77	1
Ni(II)	295	3.19	2
Co(II)	295	5.17	3
Fe(II)	295	5.43	4
Mn(II)	295	5.88	5
Cr(III)	298	3.52	3
Fe(III)	298	5.26	5

^a Number of unpaired electrons if spin free.

TABLE II
LATTICE SPACINGS OF METAL SQUARATES IN Å.

$K_2C_4O_4$	$CoC_4O_4 \cdot 2H_2O$		$MgC_4O_4 \cdot 2H_2O$		$CuC_4O_4 \cdot 2H_2O$		$CaC_4O_4 \cdot 2H_2O$		$MC_4O_4^a$ (OH)·3H ₂ O	
	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O
7.04	8.15	8.11	6.51	9.05	7.72					
4.30	6.32	6.32	5.53	8.34	6.76					
4.11	5.75	5.73	4.88	6.56	6.40					
3.74	4.69	4.47	4.28	5.70	6.16					
3.35	4.07	4.08	3.89	5.45	5.75					
3.12	3.63	3.64	3.68	4.73	5.19					
3.09	3.31	3.33	3.52	4.41	4.56					
2.97	3.18		3.31	4.16	4.25					
2.87	3.00		3.18	3.87	3.95					
2.78	2.87	2.89	3.10	3.68	3.70					
2.69	2.83		3.00	3.55	3.43					
2.62	2.71	2.72	2.73	3.37	3.25					
2.49	2.55	2.58	2.64	3.25	3.13					
2.40	2.45	2.46	2.58	3.14	3.04					
2.36	2.32	2.34	2.49	3.02	2.84					
2.20	2.25	2.27	2.47	2.84	2.74					
2.14	2.17	2.19	2.42	2.75	2.68					
2.09	2.03	2.05	2.35	2.69	2.58					
2.07	1.965	1.985	2.32	2.59	2.48					
2.04	1.911	1.937	2.26	2.50	2.41					
1.974	1.863	1.881	2.23	2.45	2.29					
1.921	1.815	1.835	2.18	2.37	2.16					
1.877	1.771	1.788	2.13	2.33	2.11					
1.816	1.727	1.745	2.09	2.26	2.06					
1.790	1.658	1.675	2.04	2.19	2.02					
1.764	1.624	1.641	1.974	2.12	1.980					
1.685	1.591	1.611	1.944	1.993	1.932					
1.665	1.562	1.578	1.899	1.936	1.851					
1.624	1.509	1.527	1.875	1.900	1.797					
1.606	1.482	1.499	1.840	1.837	1.763					
1.579	1.434	1.428	1.823	1.799	1.738					
1.563	1.415		1.798	1.751	1.704					
1.540	1.372	1.387	1.778	1.632	1.675					
1.515	1.354		1.761	1.602	1.649					
1.490	1.316		1.726	1.584						
				1.554						
				1.527						
				1.510						

^a M = Al, Fe, Cr; data measured for Fe(III) complex.

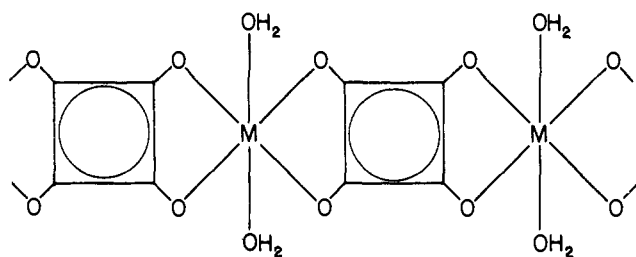


Fig. 1.—Proposed structure for squarate complexes of Mg^{++} , Mn^{++} , Fe^{++} , Co^{++} , Ni^{++} , and Zn^{++} .

The infrared spectra of the squarate complexes differ substantially from those of the corresponding croconates and provide important structural clues. The squarate spectra are very simple, showing only four bands in the sodium chloride region. The spectra are dominated by the extremely broad and strong band extending over the region $1400\text{--}1700\text{ cm.}^{-1}$. This band can be assigned to a mixture of C-C and C-O stretching vibrations. Other bands are found at 1150 and 1105 cm.^{-1} , the latter giving rise to a weak overtone at 2210 cm.^{-1} . The absence of a sharp band above 1600 cm.^{-1} indicates that probably all of the C-O groups are coordinated to metal atoms, and the great simplicity indicates that the D_{4h} symmetry of the squarate ion⁶ is not greatly reduced in the divalent complexes. Copper(II) squarate shows additional bands at 1360 , 1320 , 985 , and 900 cm.^{-1} , indicating that this compound probably has a less symmetrical structure than the other divalent transition metal squarates.

A structure for the isostructural divalent squarates which is consistent with available experimental data is shown in Fig. 1. The proposed structure is a chain polymer in which each squarate ion is chelated to two different metal ions, giving a square planar arrangement of oxygens about the metal. Water molecules occupy the two other octahedral positions about the metal atom. The divalent metal croconates have a related polymeric structure.⁵

Trivalent Metal Squarates.—Complexes of squarate ion with Al(III), Fe(III), and Cr(III) having the general formula $MC_4O_4(OH)\cdot(H_2O)_3$ were also easily obtained from aqueous solution. Like the analogous series of croconate complexes these three compounds are isostructural as shown by the X-ray powder diffraction patterns (Table II), which are identical within limits of experimental error. The infrared spectra are also quite similar, all showing bands at 3250 , 1615 , 1150 , 1105 , 1090 , 1040 , and 900 cm.^{-1} . The magnetic moments of the Cr(III) and Fe(III) compounds are slightly lower than expected for high-spin complexes of these metals (Table I). The croconate complexes of the same metals also show reduced paramagnetism, and the discussion given in the previous paper also applies here.⁵

Experimental

Nickel(II) Squarate Dihydrate.—One gram (0.09 mole) of dipotassium squarate in 10 ml. of water was added to 2.2 g. (0.09

mole) of nickel(II) chloride hexahydrate in 10 ml. of water at room temperature. A green solid precipitated immediately and the amount of solid increased as the solution was evaporated on a steam-bath to a volume of about 5 ml. The product, a finely-divided green powder, was separated by filtration and washed successively with hot water, acetone, and ether, and finally dried at room temperature and 0.05 mm. pressure for 48 hr. The yield was 1.7 g. (91%).

Anal. Calcd. for $NiC_4O_4\cdot 2H_2O$: C, 23.28; H, 1.95. Found: C, 23.12; H, 2.12.

Other Divalent Metal Squarate Dihydrates.—Calcium, cobalt(II), iron(II), magnesium, and manganese(II) squarate dihydrates were obtained in preparations similar to that described above for the nickel(II) derivative. A similar method was employed in the synthesis of copper(II) squarate dihydrate except that diketocyclobutenediol was used as the source of squarate ion. Cobalt(II), copper(II), iron(II), and manganese(II) squarate dihydrates formed pink, green, yellow, and pale pink crystals, respectively, whereas the calcium and magnesium salts were colorless. The yields were nearly quantitative except for that of iron(II) squarate, which was about 75%.

Anal. Calcd. for $CaC_4O_4\cdot 2H_2O$: C, 25.53; H, 2.14. Found: C, 25.80; H, 2.36. Calcd. for $CuC_4O_4\cdot 2H_2O$: Cu, 30.02; C, 22.70; H, 1.91. Found: Cu, 29.73; C, 22.93; H, 2.12. Calcd. for $FeC_4O_4\cdot 2H_2O$: Fe, 27.39; C, 23.56; H, 1.98. Found: Fe, 26.73; C, 23.61; H, 2.28. Calcd. for $MgC_4O_4\cdot 2H_2O$: Mg, 14.11; C, 27.86; H, 2.33. Found: Mg, 13.86, 13.90; C, 27.66, 27.81; H, 2.57, 2.69. Calcd. for $MnC_4O_4\cdot 2H_2O$: C, 23.66; H, 1.99. Found: C, 23.41; H, 2.18.

Hydroxoaluminum Squarate Trihydrate.—Aluminum nitrate enneahydrate (3.85 g., 0.01 mole) dissolved in 10 ml. of water was added to a solution of 1.1 g. (0.01 mole) of diketocyclobutenediol in 50 ml. of water. A white solid precipitated immediately. Water was evaporated to a volume of about 10 ml. on a steam-bath. The white solid was then filtered and washed with hot water, acetone, and ether, and dried *in vacuo*. The yield was 2.0 g., nearly quantitative. The same results were obtained when disodium squarate was used in place of diketocyclobutenediol.

Anal. Calcd. for $AlC_4O_8H_7$: Al, 12.84; C, 22.87; H, 3.35. Found: Al, 12.60; C, 22.74, 22.79; H, 3.22, 3.41.

Hydroxochromium(III) and Hydroxoiron(III) Squarate Trihydrates.—These two complexes were prepared in the same manner as the aluminum compound. The chromium(III) and iron(III) squarates were formed in essentially quantitative yield as gray-blue and dark brown powders, respectively.

Anal. Calcd. for $CrC_4O_8H_7$: Cr, 22.04; C, 20.43; H, 3.00. Found: Cr, 21.99; C, 20.28; H, 3.17. Calcd. for $FeC_4O_8H_7$: Fe, 23.38; C, 20.10; H, 2.95. Found: Fe, 23.42; C, 20.11; H, 3.05.

Powder X-Ray Diffraction and Infrared Spectra.—Characterization by these methods was carried out as described in the previous paper.⁵

Magnetic Properties.—A Gouy balance was used in the determination of magnetic susceptibilities as described earlier. The usual diamagnetic corrections were made for the transition metal ions, water, and hydroxyl groups.⁵ The diamagnetic correction for squarate ion was established by measuring the magnetic susceptibility of dipotassium squarate and subtracting the contribution of the two potassium ions. Squarate ion was found to have a diamagnetic susceptibility of $30.6 \times 10^{-6}\text{ g.-atom at } 25^\circ$.

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(6) M. Ito and R. West, *J. Am. Chem. Soc.*, **85**, 2580 (1963).