

during a machine malfunction. Positional and thermal parameters are given in Tables 1 and 2.

Discussion. The atom labelling sequence is given in Fig. 1. The bond distances and angles for the cation are given in Table 3. The intermolecular connectivity consists primarily of hydrogen bonding through the chloride ions, linking ammine (and amido) nitrogen atoms. Information relating to the hydrogen-bonding network is given in Table 4. The hydrogen atom H(4) on N(2) and the water hydrogen atom H(15) appear to form weak bifurcated hydrogen bonds. However, both bifurcated bonds involve the disordered nitrito oxygen atom O(2) and the possibility remains that N(2) and the water are bonded to O(2) when the O(2) site is occupied and to Cl(2) when it is not. The hydrogen bonds formed by H(8) and H(16) are also weak. The anisotropic temperature factors of the water oxygen atom, O(3), are large. The observed and calculated densities using the stoichiometry $[\text{Co}_2(\text{NH}_3)_8(\text{NH}_2)(\text{NO}_2)]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ are consistent and partial occupancy of the O(3) site is not indicated. Rather, we suspect that the disorder associated with the atom O(2) is transferred to the O(3) atom through the hydrogen atom H(15) and that the missing hydrogen atom is also disordered.

The structure of monoclinic μ -amido- μ -nitrito-bis-[tetraamminecobalt(III)] tetrachloride tetrahydrate has been reported earlier (Thewalt & Marsh, 1970). The geometry of the cation in the tetrahydrate is not significantly different from that in the dihydrate. It is possible that the latter is the orthorhombic form reported by Werner (1910) to be a monohydrate. The dihydrate is presently being used to study the electron paramagnetic resonance of μ -amido- μ -superoxo-bis-[tetraamminecobalt(III)]⁴⁺ in solid solution.

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Tris-(1,3-propanedionato)chromium(III)

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Abstract. Tris-(1,3-propanedionato)chromium(III), the simplest transition-metal 1,3-diketonate chelate, is monoclinic, $P2_1/c$, $a = 10.803$ (8), $b = 8.121$ (5), $c = 14.583$ (9) Å, $\beta = 120.24$ (3)°, $\rho_{\text{calc}} = 1.60$ g cm⁻³, $\rho_{\text{meas}} = 1.58$ g cm⁻³. The molecule has crystallographic symmetry 2 and idealized symmetry 32.

Introduction. The chelates of 1,3-diketonates have been studied extensively for a variety of reasons. One reason

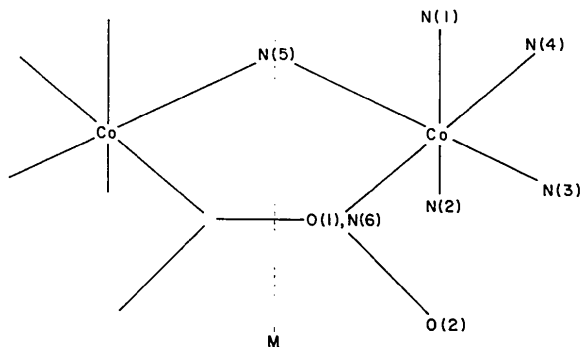


Fig. 1. Atom labelling scheme for the cation. Oxygen atom O(2) is assumed to be bonded to nitrogen atom N(6).

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References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
- DAVIES, R., MORI, M., SYKES, A. G. & WEIL, J. A. (1970). *Inorg. Synth.* 12, 197–214.
- International Tables for X-ray Crystallography* (1969). Vol. 1, 2nd ed. Birmingham: Kynoch Press.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
- STONE, M. E., ROBERTSON, B. E. & STANLEY, E. (1971). *J. Chem. Soc. (A)*, pp. 3632–3636.
- THEWALT, U. & MARSH, R. E. (1970). *Inorg. Chem.* 9, 1604–1610.
- WERNER, A. (1910). *Liebigs Ann.* 375, 1–144.

for continuing interest in these systems is the ease with which the ring substituents may be varied, resulting in dramatic changes in the chelate's physical properties. Spectral transitions in the visible region, for example, are affected by the nature of the substituent groups. Spectral shifts brought about by substituent group changes are generally explained in terms of the groups' electronic effects. Although a large number of 1,3-diketonate chelate structures have been reported, no

structural information is available for the simplest system containing the ligand 1,3-propanedione in which all substituents are hydrogen. Thus, on the usual relative scale the electronic effects are defined as zero and the structural parameters reflect the simplest of all electronic situations without the perturbing effects of groups such as CH_3 , $\text{t-C}_4\text{H}_9$, C_6H_5 , CF_3 , etc. The only known chelate of this reactive ligand is tris-(1,3-propanedionato)chromium(III), the structure of which is reported in this paper.

The compound was prepared by the method of Collman, Kittelman, Hurt & Moore (1966) and recrystallized from petroleum spirit. The resulting transparent maroon crystals are trigonal-prismatic in shape. The crystal studied was $0.038 \times 0.042 \times 0.042$ cm along the triangular edges and 0.045 cm in height.

Cell dimensions and intensities were determined on a Picker card-controlled diffractometer with Zr-filtered

Mo $K\alpha$ radiation. Photographs showed the systematic absence of $l=2n+1$ for $h0l$ data; crystals did not exhibit piezoelectricity.

For data collection, the θ - 2θ technique was used with a take-off angle of 2.7° , a crystal-to-counter distance of 33.9 cm, a scan rate of 2° min^{-1} , a minimum scan range of 2° and background counts of 10 s at each end of the scan. The procedures and weighting scheme used were those reported by Radonovich & Glick (1971). Of the 2108 unique reflexions with $\sin \theta/\lambda < 0.5958$ in the quadrant $\pm h, k, l$ 1421 were found to have net intensities greater than 2.5 standard deviations and were considered observed.

The structure was solved assuming the centrosymmetric space group, $P2_1/c$. The positions of the chromium atoms were determined from an E map phased by the Sayre equation and the other atomic positions resulted from a Fourier map phased with the chromium positions. Least-squares refinement including anisotropic thermal parameters resulted in a conventional discrepancy index of 0.054, a weighted discrepancy index of 0.068 and an error of fit of 2.6.* A final difference map contained peaks corresponding to some, but not all, of the hydrogen positions.

Table 1. Atomic parameters of tris-(1,3-propanedionato)chromium(III)

The estimated errors in the last digit reported are given in parentheses. The anisotropic thermal expression was $\exp \{- (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})\}$.

Values are $\times 10^4$.

	x	y	z
Cr(A)	5000	4908 (1)	2500
O(A1)	3871 (4)	6607 (5)	2704 (3)
O(A2)	6382 (4)	4896 (5)	4025 (3)
O(A3)	3808 (4)	3243 (5)	2647 (3)
C(A1)	4010 (5)	8171 (7)	2680 (4)
C(A11)	5000	8964 (10)	2500
C(A2)	6281 (8)	4021 (9)	4730 (5)
C(A3)	4016 (7)	2599 (8)	3522 (5)
C(A23)	5171 (8)	2936 (9)	4515 (5)
Cr(B)	0	666 (1)	7500
O(B1)	749 (4)	2357 (5)	6950 (3)
O(B2)	1802 (4)	667 (5)	8844 (3)
O(B3)	819 (4)	-985 (5)	6986 (3)
C(B1)	678 (6)	3916 (8)	7028 (4)
C(B11)	0	4716 (1)	7500
C(B2)	2098 (7)	-221 (10)	9646 (5)
C(B3)	205 (8)	-1659 (7)	6058 (6)
C(B23)	1199 (9)	-1317 (10)	9748 (5)

Discussion. The molecules are located upon crystallographic twofold axes; thus there are two independent half-molecules possessing crystallographic 2 symmetry, with approximate 32 molecular symmetry. The atomic labeling is shown in Fig. 1 and the packing is shown in Fig. 2. Tables 1 and 2 contain the atomic parameters and bond distances.

The deviations from 32 symmetry are less than 12 e.s.d. The ligands are planar within experimental error. The displacements from the basal planes along the

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30784 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 (cont.)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr(A)	87 (1)	152 (2)	64 (9)	0 (-)	34 (9)	0
O(A1)	125 (5)	214 (9)	116 (4)	16 (5)	80 (4)	6 (4)
O(A2)	127 (5)	259 (9)	75 (3)	-16 (5)	28 (3)	-25 (4)
O(A3)	135 (5)	201 (8)	92 (3)	-38 (5)	52 (3)	-2 (4)
C(A1)	125 (8)	160 (1)	69 (4)	14 (7)	37 (4)	2 (5)
C(A11)	119 (1)	195 (2)	74 (6)	0	48 (7)	0
C(A2)	186 (10)	271 (17)	74 (5)	59 (10)	45 (6)	-3 (7)
C(A3)	214 (11)	189 (12)	95 (5)	26 (9)	89 (7)	18 (7)
C(A23)	213 (1)	263 (2)	91 (6)	-1 (10)	64 (7)	74 (7)
Cr(B)	90 (2)	140 (2)	59 (1)	0 (-1)	32 (1)	0
O(B1)	143 (5)	166 (8)	99 (3)	18 (5)	71 (4)	77 (4)
O(B2)	112 (5)	267 (9)	68 (3)	-2 (5)	28 (3)	-4 (4)
O(B3)	171 (6)	175 (8)	96 (4)	45 (5)	71 (4)	13 (4)
C(B1)	140 (8)	183 (13)	85 (5)	43 (8)	44 (5)	11 (6)
C(B11)	187 (15)	199 (20)	121 (9)	0	79 (10)	0
C(B2)	176 (10)	303 (17)	72 (5)	46 (10)	49 (6)	1 (7)
C(B3)	255 (12)	175 (12)	90 (5)	-19 (10)	99 (7)	-10 (7)
C(B23)	242 (13)	293 (17)	75 (5)	16 (12)	58 (7)	17 (7)

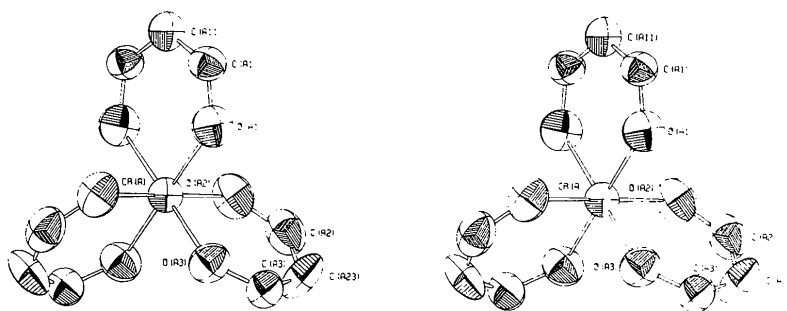


Fig. 1. Atomic labeling.

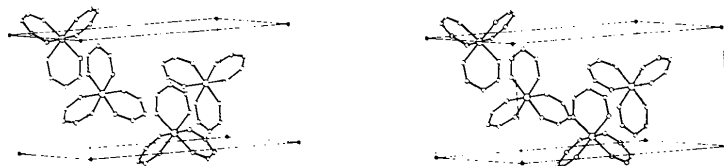


Fig. 2. Arrangement of atoms in the unit cell.

Table 2. Intramolecular bond lengths (Å) in tris-(1,3-propanedionato)chromium(III)

Cr(A)—O(A1)	1.962 (4)	Cr(B)—O(B1)	1.961 (4)
Cr(A)—O(A2)	1.945 (4)	Cr(B)—O(B2)	1.955 (4)
Cr(A)—O(A3)	1.954 (4)	Cr(B)—O(B3)	1.931 (4)
O(A1)—C(A1)	1.282 (6)	O(B1)—C(B1)	1.270 (7)
O(A2)—C(A2)	1.299 (8)	O(B2)—C(B2)	1.286 (7)
O(A3)—C(A3)	1.287 (6)	O(B3)—C(B3)	1.272 (7)
C(A1)—C(A11)	1.384 (7)	C(B1)—C(B11)	1.399 (7)
C(A2)—C(A23)	1.389 (9)	C(B2)—C(B23)	1.392 (9)
C(A3)—C(A23)	1.372 (8)	C(B3)—C(B23)	1.377 (9)

twofold axes are <0.001 Å in molecule *B* and ~ 0.04 Å in molecule *A*.

The Cr—O distance of 1.95 Å is equal to that found in the tris(acetylacetonato)chromium(III) complex

(Morosin, 1965). In Table 3, the chelate ring parameters of tris-(1,3-propanedionato)chromium(III) are compared with those of some trivalent acetylacetonates (Lingafelter & Braun, 1966). In all cases the results are consistent with π -electron delocalization throughout the diketonate ring.

The striking structural similarities between the chromium(III) chelates of acetylacetonate and 1,3-propanedione would lead one to believe that the electronic structures are practically indistinguishable. However, there are important spectral (Forster, 1966; Fatta & Lintvedt, 1971) and electrochemical differences (Handy & Lintvedt, 1974) which have been attributed to the different electronic effects of the substituent groups, *i.e.* H vs CH_3 . The spectral shifts are small but significant. The reduction potentials, on the other hand, differ by 0.41 V.

Table 3. A comparison of parameters with trivalent acetylacetonates

Compound	Distances (Å)			Bite size O...O
	C—C	C—O	M—O	
1. Cr(1,3-propanedionato) ₃	1.38	1.28	1.95	2.80
2. Cr(acetylacetonato) ₃	1.39	1.26	1.95	2.79
3. Co(acetylacetonato) ₃	1.38	1.27	1.98	2.85
4. Fe(acetylacetonato) ₃	1.38	1.26	1.99	2.74

	Angles (°)			
	M—O—C	O—C—C	C—C—C	O—M—O
1.	126.3	125.4	124.7	91.4
2.	127	125	125	91.1
3.	121.8	127.5	123.6	97.3
4.	129.3	125	124.8	87.1

References

- COLLMAN, J. P., KITTELMAN, E. T., HURT, W. S. & MOORE, N. S. (1966). *Inorg. Synth.* **8**, 141–148.
 FATTA, A. M. & LINTVEDT, R. L. (1971). *Inorg. Chem.* **10**, 478–481.
 FORSTER, L. S. (1966). *Transition Metal Chemistry*, Vol. 5, Chap. 1, pp. 1–45. New York: Marcel Dekker.
 LINGAFELTER, E. C. & BRAUN, R. L. (1966). *J. Amer. Chem. Soc.* **88**, 2951–2956.
 HANDY, R. F. & LINTVEDT, R. L. (1974). *Inorg. Chem.* **13**, 893–896.
 MOROSIN, B. (1965). *Acta Cryst.* **19**, 131–137.
 RADONOVICH, L. J. & GLICK, M. D. (1970). *Inorg. Chem.* **10**, 1463–1468.