Notes

Malonato(ethylenediamine) Complexes of Chromium(III): The Structure of Di-μ-hydroxo-bis[(ethylenediamine)malonatochromium(III)]

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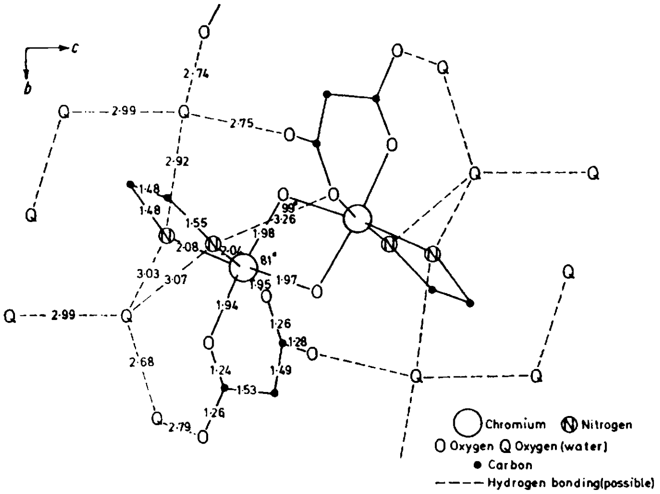
In the preparation of new malonatoethylenediamine complexes of chromium(III) for kinetic investigations the bridged dimer [{Cr(en)(mal)(OH)}$_2$] has been isolated. The preparation of two other complexes and the crystal structure of the dimer are reported, and the relevance of the structure is discussed with respect to both kinetic and magnetic coupling studies with chromium(III).

IN work with amine and ammine complexes of chromium(III) I have been interested in the labilization of chromium–nitrogen bonds by other ligands, particularly oxalate.[1-3] In order to extend this work, the complexes [Cr(en)$_2$(mal)][ClO$_4$] and K[Cr(en)(mal)$_2$] were recently prepared.[4,†] A neutral complex was also obtained which was formulated as [Cr(en)(mal)(OH)(OH$_2$)]·2H$_2$O. I report here the results of a crystal-structure determination on this compound.

RESULTS

The structure determination showed the neutral complex to be the dimer, di-μ-hydroxo-bis[(ethylenediamine)malonatochromium(III)] hexahydrate, [{Cr(en)(mal)(OH)}$_2$].6H$_2$O. A projection of the structure down the short, *a*, axis is shown in the Figure, and atomic co-ordinates are given in Table 1.



Projection of the structure of [{Cr(en)(mal)(OH)}$_2$]·6H$_2$O, down the *a* axis. Bond lengths (Å) are marked

The structure has a centre of symmetry at the centre of the di-μ-hydroxo-bridge. All bond lengths and angles are close to those recorded for related complexes.[5,6] The chromium–chromium distance is also within the range found for other di-μ-hydroxo-bridged complexes but appears slightly shorter [3.003(6)Å] than for the bis(malonato), 3.05 Å, and bis(ethylenediamine), 3.03 Å, complexes, which may have a significant effect on the magnetic coupling of the chromium atoms.

TABLE 1

Unique atom co-ordinates for [{Cr(en)(mal)(OH)}$_2$]·6H$_2$O

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cr	0 953 4(6)	0 563 2(3)	0 430 9(2)
O(1)	0 922(2)	0 383(1)	0 479(1)
Ethylenediamine			
N(1)	0 840(3)	0 480(2)	0 339(1)
N(2)	1 246(3)	0 502(2)	0 394(1)
C(4)	1 195(5)	0 389(2)	0 339(1)
C(5)	1 029(4)	0 456(2)	0 294(1)
Malonate			
O(2)	1 000(2)	0 744(1)	0 389(1)
O(3)	0 663(2)	0 623(1)	0 459(1)
O(4)	0 985(2)	0 974(1)	0 384(1)
O(5)	0 458(3)	0 769(1)	0 513(1)
C(1)	0 631(4)	0 745(2)	0 480(1)
C(2)	0 930(4)	0 859(2)	0 409(1)
C(3)	0 777(4)	0 867(2)	0 470(1)
Water			
O(A)	0 323(3)	0 828(2)	0 644(1)
O(B)	0 507(3)	0 177(2)	0 212(1)
O(C)	0 605(4)	0 436(2)	0 172(1)

The configuration of ligands about the chromium atoms can be regarded as giving pairs of left- and right-handed propellers in each dimer. The pseudo-three-fold axes of the propellers lie close to the short, *a*, axis of the crystal (*cf.* the structure in ref. 7). The carbon–carbon bond of the ethylenediamine is almost perpendicular to the propeller axis (configurations Λλ and Δδ).[8] There was no evidence from Fourier-difference maps for the alternative parallel configuration of this bond.[9] No attempt was made at this stage to locate hydrogen atoms attached to nitrogen or the independent water molecules, but it is likely that the ethylenediamine configuration is largely determined by hydrogen bonding since there can be little or no intramolecular stereochemical restraint on its configuration.

A survey of contact distances and angles about the dimer and the water oxygens suggests a network of hydrogen

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† The following abbreviations are used in this paper: en = 1,2-diaminoethane (ethylenediamine); mal = propanedioate (malonate); ox = ethanedioate (oxalate).

bonds involving amine nitrogen, malonate oxygen, and the water, which serves to bind the whole structure together. Some of the most likely positions for hydrogen bonds are indicated in the Figure.

DISCUSSION

The structure of this complex is of interest for a number of reasons. It is an interesting addition to the series of complexes which have been used for a study of magnetic coupling[5] and it is the first such complex containing different chelating ligands on a single chromium centre.

Secondly the determination of this structure together with the closely similar electronic spectra of this dimer and of the monomeric ion, $[Cr(en)(mal)(OH_2)_2]^+$, would be in agreement with a *cis* configuration of the latter. The spectra of these complexes and some other complexes of interest are compared in Table 2.

TABLE 2

Spectroscopic parameters for some chromium(III) complexes

Complex	$\lambda_{max.}$/nm [a]	Ref.
$[Cr(en)_2(mal)]^+$	378(62), 503(86)	*b*
$[Cr(en)_2(ox)]^+$	372(85), 496(91)	*c*
$[Cr(en)(mal)(OH_2)_2]^+$	395(38), 525(53)	*b*
$[\{Cr(en)(mal)(OH)\}_2]$	395(56), 544(66)	*b*
$[Cr(en)(ox)(OH_2)_2]^+$	394(63), 524(60)	*c*
$[Cr(en)(ox)(OH)(OH_2)]$	396(55), 542(58)	*d*
$[Cr(en)(mal)_2]^-$	393.5(59), 529(66)	*b*
$[Cr(en)(ox)_2]^-$	394(100), 530(92)	11

[a] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] This work. [c] M. B. Davies and J. W. Lethbridge.[13] [d] Diffuse-reflectance spectrum (peak heights are relative only), M. B. Davies and J. W. Lethbridge, unpublished work.

Thirdly the characterization of this dimer provides evidence for the likely dimeric structure of the insoluble purple complex first noted by Werner[10] as a secondary product of reactions of chromium(III) complexes involving both ethylenediamine and oxalate. This complex, formulated by Werner as the neutral monomer, $[Cr(en)(ox)(OH)(OH_2)]$, has a physical appearance very similar to that of a sample of the present dimer dehydrated by immersion in alcohol, and its electronic spectrum is also similar to that of the dimer. The insolubility and kinetic inertness of the insoluble purple compound would be remarkable for a monomer which differed only by a proton from the very soluble ion $[Cr(en)(ox)(OH_2)_2]^+$, but would be in agreement with its formulation as a bridged dimeric complex. Again a bridge formulation for this complex would be in agreement with and provide additional evidence for the *cis* configuration of the ion $[Cr(en)(ox)(OH_2)_2]^+$ formed during the aquation of both $[Cr(en)_2(ox)]^+$ and $[Cr(en)(ox)_2]^-$ ions.[1,11]

The *cis* configuration shown about the chromium in the present case provides further evidence for the retention of configuration during the aquation of *cis*-amines or -ammines. It has been suggested that these reactions occur by an associative mechanism, I_a, using hydrogen bonding to the co-ordinated water, without separation of neighbouring co-ordinated nitrogen atoms.[12] Finally, the isolation of this complex also shows clearly that dimerization reactions cannot be ignored when considering possible reaction paths for aquachromium(III) complexes if the pH is allowed to rise above 4.

EXPERIMENTAL

Complex Preparation.—The double complex $[Cr(en)_2(mal)][Cr(en)(mal)_2]$ was prepared by a method analogous to that used for the corresponding oxalate complex.[14] The starting material, $K[Cr(mal)_2(OH_2)_2]$, was prepared in solution by the reaction of malonic acid (50 g) with potassium dichromate (23.54 g). Ethylenediamine (30 cm^3) was added with stirring to this solution (100 cm^3) and the reaction mixture warmed on a steam-bath for 30 min. On cooling a red solid separated which was the impure double complex. A saturated aqueous solution of the solid product (6 g, 25 cm^3) was passed successively through ion-exchange columns (Deacidite FFDVB, chloride form; and Dowex 50W, potassium form) and a pale purple eluate was finally obtained from which bright red crystals of $[\{Cr(en)(mal)(OH)\}_2]\cdot 6H_2O$ (0.05 g, 1%) were deposited on standing at room temperature (Found: C, 20.7; H, 4.9; N, 10.0. Calc. for $C_{10}H_{34}Cr_2N_4O_{16}$: C, 21.05; H, 5.95; N, 9.80%).

Bis(ethylenediamine)malonatochromium(III) *Perchlorate.*—The saturated solution of the double complex was passed only through the anion-exchange column and the red-orange eluate obtained was reduced in volume by evaporation at 60 °C in a stream of dry air. Solid lithium perchlorate (6 g) was added to the concentrated solution (10 cm^3) to precipitate the perchlorate salt of the complex, which was recrystallized from water, yield 1 g (25%) (Found: C, 22.6; H, 5.3; N, 14.5. Calc. for $C_7H_{18}ClCrN_4O_8$: C, 22.5; H, 4.85; N, 15.0%).

Potassium (Ethylenediamine)bis(malonato)chromate(III)–*Potassium Iodide* (1/1).—The ion $[Cr(en)(mal)_2]^-$ retained on the anion-exchange column above was eluted using potassium chloride (1 mol dm^{-3}). The eluate was concentrated (25 cm^3) at 60 °C and the complex crystallized out by addition of solid potassium iodide (25 g) followed by cooling in ice, yield 1.5 g (27%) (Found: C, 18.3; H, 2.9; N, 5.3. Calc. for $C_8H_{12}CrIK_2N_2O_8$: C, 18.45; H, 2.3; N, 5.35%).

Structure Determination of Di-μ-hydroxo-bis[(ethylenediamine)malonatochromium(III)] *Hexahydrate.*—*Crystal data.* $C_{10}H_{34}Cr_2N_4O_{16}$, $M = 570.39$, Monoclinic, space group $P2_1/c$, $a = 6.19(1)$, $b = 9.61(2)$, $c = 19.47(3)$ Å, $\beta = 90.57(5)°$, $D_m = 1.632$ g cm^{-3}, $Z = 2$, $U = 1\,158(6)$ Å^3, $D_c = 1.635$ g cm^{-3}, $F(000) = 595.97$, λ(Cu-K_α, filtered) $= 1.542$ Å, $\mu = 83.5$ cm^{-1}.

Intensity data were collected using multiple-film-pack Weissenberg photography, ($hk0$) to ($hk3$), and the films processed using the S.R.C. Microdensitometer Service. Reflections were measured up to $2\theta = 105°$. A total of 1 053 reflections were recorded; reflections were only treated as observed where the integrated intensities could be computed with an accuracy better than 5%. These reflections were merged to give 426 unique reflections. On the basis of agreement between merged reflections a final structure-factor agreement of 7.4% was predicted. Calculation was carried out using the SHELX program.[15] The heavy-atom technique was used and the Patterson map clearly showed the two chromium atoms of the dimer located on either side of the centre of symmetry. Anisotropic thermal vibration was assumed only for chromium; using full-matrix least squares, convergence was reached after six cycles with a conventional value of $R = 0.073$.

At this stage 13 reflections remained with deviations in F_c greater than 2σ, of which three could be traced to inconsistent film data. Correlation of data for the ranges of h, k, and l and between different $(\sin \theta)/\lambda$ ranges showed no significant inconsistencies. An absorption correction was not applied but was expected to be small for the crystal used ($0.33 \times 0.18 \times 0.07$ mm).

Tables of structure factors, thermal parameters, and bond lengths and angles are available as Supplementary Publication No. SUP 22833 (6 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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