

TRIAMMINE COBALT(III)-L-MALATE. MALATE ION AS A TRIDENTATE LIGAND

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Abstract—The crystal structure of the title compound has been determined from single crystal X-ray diffraction data. There is little angle strain in the complex which has two carboxylate ions and one alkoxide ion bound to cobalt(III). These conclusions agree with IR, CD and NMR spectral data except that ^1H coupling constants show that the conformation of the malate ligand differs slightly in solid and solution. The three ammonia ligands have different ^1H chemical shifts and different rates of hydrogen exchange in D_2O .

The reaction of the L-malate ion with a tetraamine *cis*-diaquo complex of cobalt(III) at pH 7 gives a crystalline product whose empirical formula is $[\text{Co}(\text{NH}_3)_3\text{-L-malate}] \cdot 2\text{H}_2\text{O}$ (1). It is non-ionic, based on conductivity and chemical analysis, suggesting that cobalt binds to a tridentate malate trianion through two carboxylate and one alkoxide oxygen.¹ Such a structure is consistent with the CD spectra in solution and the IR spectra of the solid. There is considerable evidence, based largely on spectroscopic or analytical evidence, for binding of alkoxide ions in complexes of hydroxyacids.² For example, mixed bis-phenanthroline-malate complexes of Co^{III} $-\text{CO}_2^-$ and $-\text{O}^-$ form a five-membered ring with hydrogen bonding of the second carboxylic residue to the alkoxide oxygen.³ The X-ray diffraction evidence on copper(II)-tartrate complexes demonstrates complexing to the alkoxide oxygen.⁴ Some of these complexes are polynuclear and in others the metal is bound to one alkoxide and one carboxylate group. Sugars form ammine complexes with cobalt(III) but binding is by hydroxyl rather than alkoxide groups.⁵

The proposed structure of 1 is reasonable, but unproven; chemical analysis, for example, is con-

sistent with the malate ion acting as a bidentate ligand and with OH^- complexed to cobalt(III). We therefore examined the structure in solution by NMR spectroscopy and in the crystal by X-ray diffraction.

RESULTS AND DISCUSSION

Structure in the crystal

The L-malate trianion is bound to the cobalt atom through O(1A), O(2A) and O(4A) forming five- and six-membered rings; the numbering scheme is shown in Fig. 1. O(4B) of the L-malate ligand is hydrogen bonded to water, H_2O (9), which is hydrogen bonded to the other water molecule, H_2O (8). Hydrogen bonds between water solvates related by the 2_1 axes parallel to the *c* axis result in helical "chains" of molecules along the *c* direction. Hydrogen bonds between water and O(2A) of the L-malate related by the 2_1 axes parallel to the *b* axis result in interactions between the "chains".

Bond lengths and angles between heavy atoms are given in Table 1. (Values in parentheses are the number of standard deviations.) Complete bond distances and angles are included in the Supplementary Material. Bond angles about cobalt are

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Table 1. Selected bond distances and angles for Co(NH₃)₃(L-malate)·2H₂O

Distance (Å)	
Co(1)—O(1A)	1.926(2)
Co(1)—O(2A)	1.887(2)
Co(1)—O(4A)	1.926(2)
Co(1)—N(5)	1.938(2)
Co(1)—N(6)	1.970(2)
Co(1)—N(7)	1.947(2)
C(1)—O(1A)	1.288(3)
C(1)—O(1B)	1.241(3)
C(1)—C(2)	1.535(4)
C(2)—O(2A)	1.415(3)
C(2)—C(3)	1.528(4)
C(3)—C(4)	1.521(4)
C(4)—O(4A)	1.282(3)
C(4)—O(4B)	1.238(3)
Angle (°)	
O(1A)—Co(1)—O(2A)	85.6(1)
O(1A)—Co(1)—O(4A)	89.7(1)
O(1A)—Co(1)—N(5)	176.1(1)
O(1A)—Co(1)—N(6)	94.3(1)
O(1A)—Co(1)—N(7)	89.3(1)
O(2A)—Co(1)—O(4A)	91.8(1)
O(2A)—Co(1)—N(5)	90.5(1)
O(2A)—Co(1)—N(6)	177.6(1)
O(2A)—Co(1)—N(7)	91.6(1)
O(4A)—Co(1)—N(5)	90.3(1)
O(4A)—Co(1)—N(6)	85.8(1)
O(4A)—Co(1)—N(7)	176.4(1)
N(5)—Co(1)—N(6)	89.6(1)
N(5)—Co(1)—N(7)	90.8(1)
N(6)—Co(1)—N(7)	90.8(1)
Co(1)—O(1A)—C(1)	109.9(2)
Co(1)—O(2A)—C(2)	105.1(1)
Co(1)—O(4A)—C(4)	129.3(2)
O(1A)—C(1)—O(1B)	123.9(3)
O(1A)—C(1)—C(2)	115.1(2)
O(1B)—C(1)—C(2)	121.1(2)
O(2A)—C(2)—C(1)	109.2(2)
O(2A)—C(2)—C(3)	110.7(2)
C(1)—C(2)—C(3)	109.4(2)
C(2)—C(3)—C(4)	113.6(2)
O(4A)—C(4)—O(4B)	121.0(2)
O(4A)—C(4)—C(3)	120.1(2)
O(4B)—C(4)—C(3)	118.9(2)

close to 90°, and those for carbon and oxygen of the malate ligand are close to values typical of tetrahedral and trigonal centres, corresponding to little angle strain in the malate ligand. Figure 1 shows the structure of the complex and Fig. 2 shows it looking down the C(2)—C(3) bond.

Bond lengths of cobalt are *ca* 1.9 and 1.95 Å to oxygen and nitrogen, respectively (Table 1). The malate residue is also relatively unstrained. The bond lengths of cobalt to oxygen and nitrogen

are similar to those in L-glutamate bis(ethylenediamine)cobalt(III) perchlorate⁸ except that this has a slightly shorter bond of 1.87 Å between the cobalt and alkoxide oxygen. Bonds of cobalt to alkoxide oxygens are shorter than to carboxylate oxygens, pointing to a stronger interaction. Complexes of cobalt(III) with the bidentate malate or tartrate ion typically involve one alkoxide and one carboxylate ligand rather than two carboxylate ligands.³

The new results fit earlier evidence¹ that structures are similar in the solid and solution and formation of a complex with a tridentate malate trianion forces chirality on the cobalt centre.

NMR spectra

There are four well-defined ¹³C signals (¹H decoupled) of the complex at 75.4 and 39.3 ppm corresponding to the methine and methylene carbons, respectively, and two signals of the carboxyl carbon at 179 and 190 ppm.⁹ We measured *T*₁ values for the carboxyl carbons in order to assign the signals, and values are: 2.63 (190 ppm) and 6.41 s (179 ppm). We assume that the carboxyl residue [C(4)] in a six-membered ring (Fig. 1) will have a higher mobility and a higher *T*₁ than the carboxyl residue [C(2)] in a five-membered ring. On this basis we assign the signal at 190 ppm to C(1) and that at 179 ppm to C(4).

There are two methylene (2.4 and 2.6 ppm) and one methine (3.7 ppm) signals in the ¹H NMR spectrum in D₂O with extensive vicinal and geminal coupling and each set of signals is a doublet of doublets (Fig. 3). The chemical shifts (δ , ppm) and coupling constants (*J*, Hz) are shown in Scheme 1. We have to consider the assignments of the methylene hydrogens H(3A) and H(3B) on C(3) and their coupling with the methine hydrogen on C(2) (Fig. 3). The view of the crystal structure down the C(2)—C(3) bond (Fig. 2) shows that in the solid methine and methylene hydrogens are in an approximately staggered conformation with dihedral angles of *ca* 60°. This conformation should lead to very similar low vicinal coupling constants between the methine hydrogen and each of the methylene hydrogens,¹⁰ but instead we have very different coupling constants of *J* \approx 6 and 1 Hz (Scheme 1). This result suggests that the complex has slightly different geometries in the crystal and in solution, with a change in the dihedral angles due to rotation about the C(2)—C(3) bond (Fig. 2). Probably the H(2A)—H(3A) dihedral angle decreases from *ca* 60° in the crystal and that for H(2A)—H(3B) correspondingly increases. The coupling constants approximately fit a Karplus

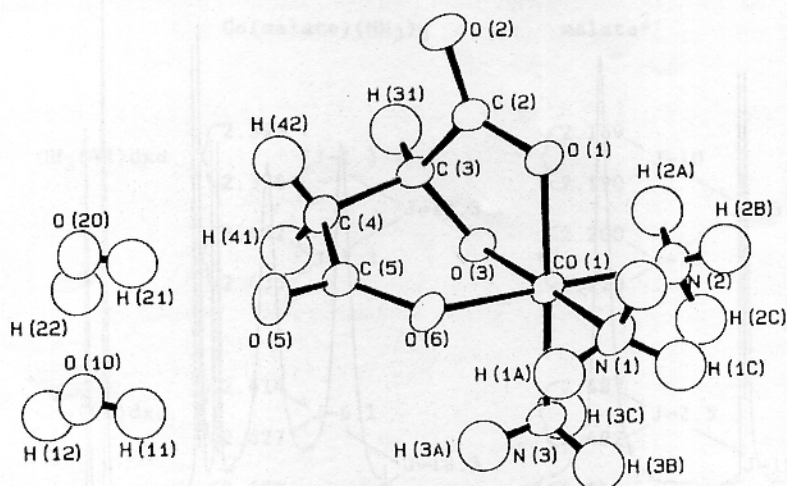


Fig. 1. ORTEP⁶ drawing of the structure of $\text{Co}(\text{NH}_3)_3(\text{L-malate}) \cdot 2\text{H}_2\text{O}$ (1) showing the atomic numbering scheme;⁷ ellipsoids are drawn at 50% probability level.

relation¹⁰ if the $\text{H}(2\text{A})\text{—H}(3\text{A})$ dihedral angle decreases in solution to $20\text{--}30^\circ$ and that for $\text{H}(2\text{A})\text{—H}(3\text{B})$ increases to $90\text{--}100^\circ$. This rotation changes the geometry of the six-membered ring in the complex. An alternative possibility is that rotation reduces the $\text{H}(2\text{A})\text{—H}(3\text{B})$ dihedral angle (Fig. 2). Inspection of models and molecular mechanics calculations (Experimental) suggests that a decrease in the $\text{H}(2\text{A})\text{—H}(3\text{A})$ bond angle is preferred (Experimental).

The conformation of the six-membered ring of the malate ligand in the crystal is probably governed in part by hydrogen bonding (Fig. 1 and Supplementary Material). These packing constraints disappear in solution permitting the observed rotation about the $\text{C}(2)\text{—C}(3)$ bond. In addition, hydrogen

bonds to water molecules in the crystal differ from those in solution. Changes in conformation on going from the solid to aqueous solution are understandable, for example, intramolecular hydrogen bonds in hydrogen malate and hydrogen phthalate ion are unsymmetrical in water, but symmetrical in the crystal.¹¹

Hydrogens of the ammonia ligands give broad, well-separated, signals (Fig. 3). Exchange with D_2O is relatively slow, and different for the three ammonias. The spectra of freshly prepared and 1-day-old solutions are compared in Figs 3A and B. There is little exchange for N—H signals at 3.43 ppm, more for those at 2.91 ppm and extensive exchange for those at 2.76 ppm. There is also line-broadening, in part due to the replacement of NH by ND. Exchange and line-broadening were very evident after 6 days and new signals appeared because of the decomposition of the complex which would generate paramagnetic cobalt(II) and cause line-broadening.

The ^1H coupling constants in the NMR spectrum of L-malate dianion (Scheme 1) fit a conformation with *anti*-carboxylate residues as shown in a Newman projection (2).

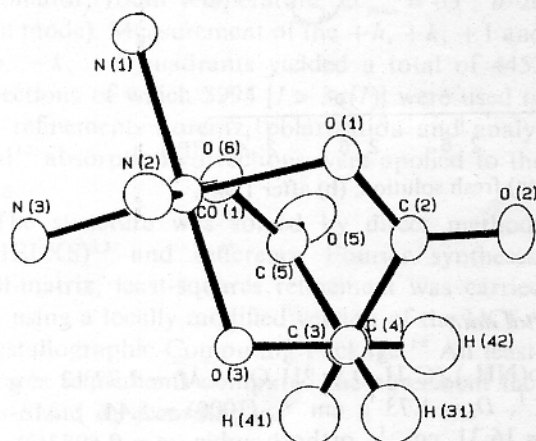
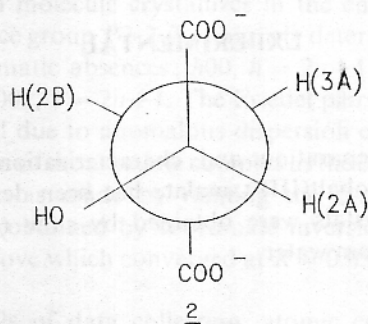


Fig. 2. ORTEP⁶ drawing of $\text{Co}(\text{NH}_3)_3(\text{L-malate}) \cdot 2\text{H}_2\text{O}$ (1) looking down the $\text{C}(3)\text{—C}(4)$ bond; ellipsoids drawn at 50% probability level. Solvate waters and ammonia hydrogens have been eliminated for clarity. Atom labels modified with PLOTMD.⁷



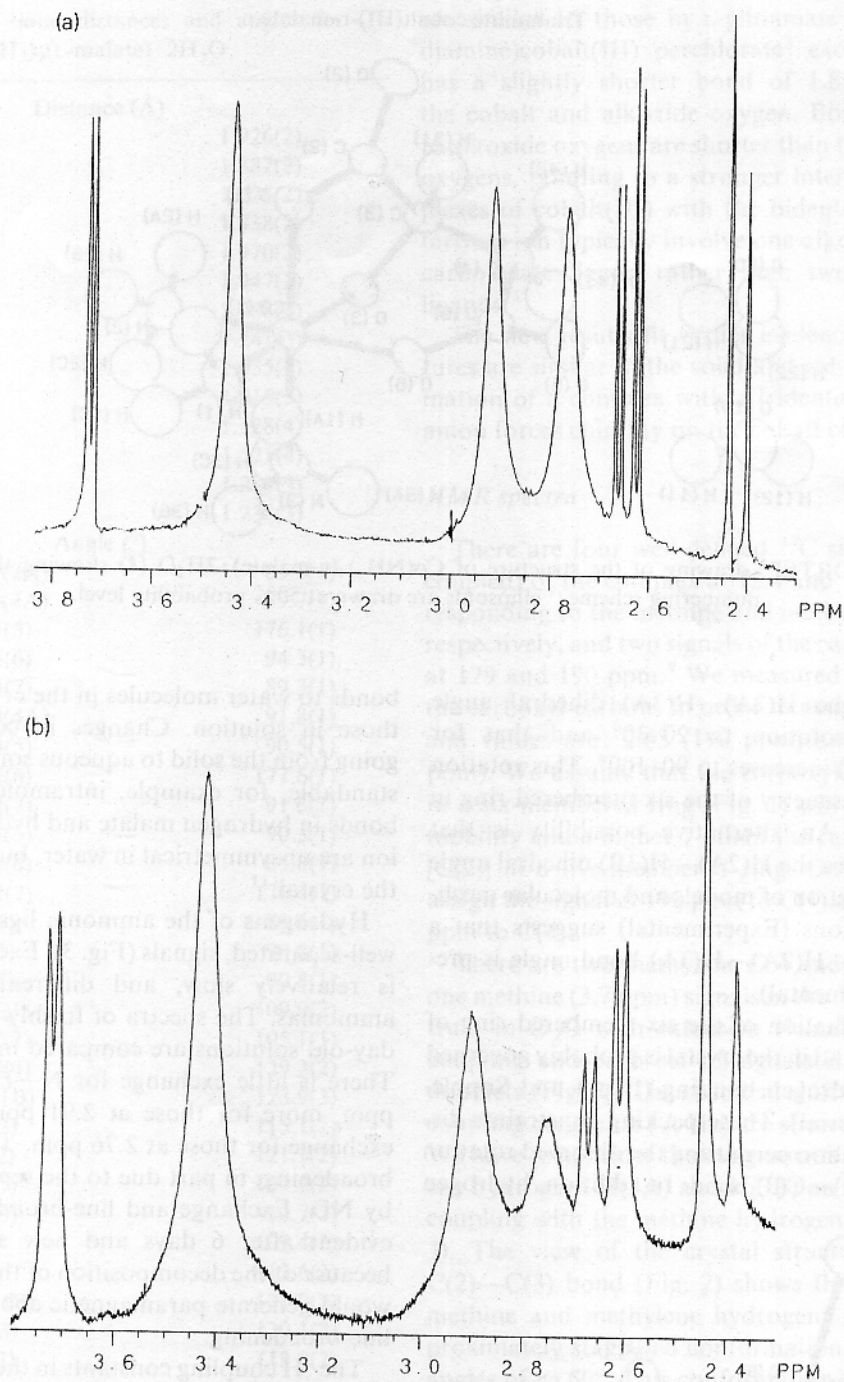


Fig. 3. ^1H NMR spectra of 0.01 M **1** in D_2O , (a) fresh solution, (b) after 1 day.

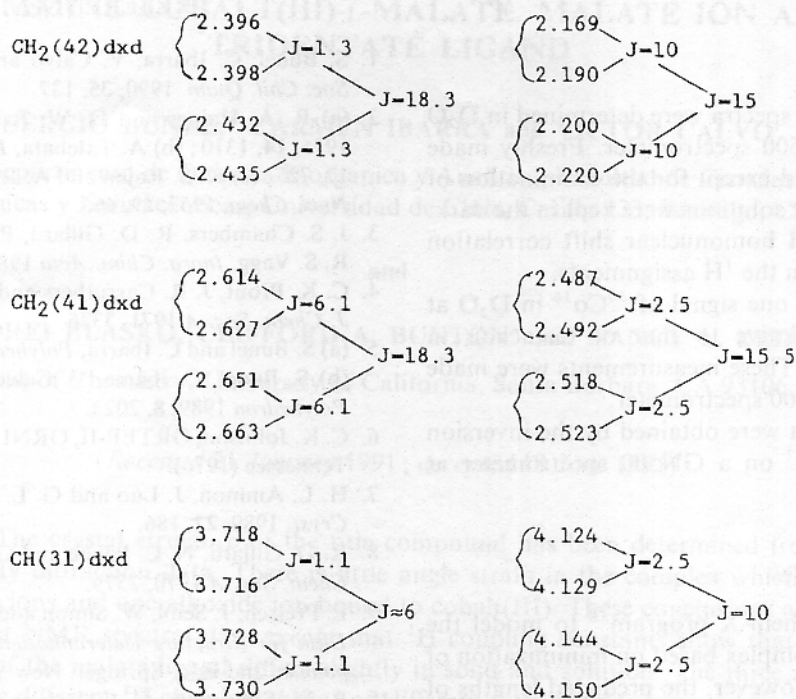
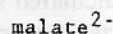
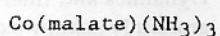
EXPERIMENTAL

Materials

The preparation and characterization of triammine cobalt(III)-L-malate has been described.¹ Single crystals were obtained by slow recrystallization from water.

Crystal data

$\text{Co}(\text{NH}_3)_3(\text{C}_4\text{H}_3\text{O}_5) \cdot 2\text{H}_2\text{O}$, $M = 2.77.12$ g mol $^{-1}$, $D_c = 1.73$ g cm $^{-3}$, $F(000) = 5.44$, $\mu(\text{Mo}-K_\alpha) = 16.31$ cm $^{-1}$, orthorhombic, $a = 9.6983(3)$, $b = 14.2528(4)$, $c = 7.6901(2)$ Å, $V = 1063(3)$ Å 3 , $Z = 4$, space group $P2_12_12_1$ (no. 19), red-violet, crystal dimensions $0.50 \times 0.30 \times 0.25$ mm.



Scheme 1.

Structure determination

Diffraction data were obtained on a Huber four-circle diffractometer automated by Crystal Logic, Inc. (Mo- K_{α} , $\lambda = 0.71073$ Å, graphite monochromator, room temperature, $2\theta_{\max} = 65^\circ$, θ - 2θ scan mode). Measurement of the $+h$, $+k$, $+l$ and $-h$, $-k$, $-l$ quadrants yielded a total of 4452 reflections of which 3994 [$I > 3\sigma(I)$] were used in the refinement. Lorentz, polarization and analytical¹² absorption corrections were applied to the data.

The structure was solved by direct methods (SHELXS)¹³ and difference Fourier syntheses. Full-matrix, least-squares refinement was carried out using a locally modified version of the UCLA Crystallographic Computing Package.¹⁴ All least-squares refinements computed the agreement factors R and R_w according to:

$$R = \frac{\sum(|F_o| - |F_c|)}{\sum(|F_o|)}$$

$$R_w = \frac{[\sum(\omega(|F_o| - |F_c|)^2) / \sum(\omega|F_o|^2)]^{1/2}}{2}$$

where F_o is the observed structure factor, F_c is the calculated structure factor, and $\omega = 1/(\sigma(F_o))^2$.

Scattering factors and corrections for anomalous dispersion were taken from the International Tables for X-ray Crystallography.¹⁵ Positions and anisotropic thermal parameters were allowed to vary for all non-hydrogen atoms. Hydrogens were assigned thermal parameters of 0.05 Å², those of the solvent water molecules were located in difference maps and their positions allowed to refine; those bonded to nitrogen or carbon were fixed at calculated positions. The final refinement of 148 parameters converged at $R = 0.046$ and $R_w = 0.060$ with EOF = 1.98. The final difference map contained no significant features.

The chiral molecule crystallizes in the enantiomorphic space group $P2_12_12_1$, uniquely determined by the systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. The Friedel pairs were not averaged due to anomalous dispersion effects. Confirmation of the L-malate complex as the correct enantiomer was made by refining the D-malate enantiomer (obtained by coordinate inversion) as described above which converged at $R = 0.057$ and $R_w = 0.078$.

Full details of data collection, atomic coordi-

nates, thermal parameters, full bond length and angle data, and observed and calculated structure factors have been deposited as supplementary material with the Editor, from whom copies are available on request.

NMR spectra

The ^1H and ^{13}C spectra were determined in D_2O at 25°C in a GN500 spectrometer. Freshly made solutions were used except for the examination of NH exchange. The solutions were kept in the dark. We used a 2D ^1H homonuclear shift correlation (COSY) to confirm the ^1H assignments.

There was only one signal of $^{59}\text{Co}^{16}$ in D_2O at -2445.5 ppm relative to that of $\text{Co}(\text{acac})_3$ in CD_3OD (0 ppm). These measurements were made at 25°C on a GN300 spectrometer.

The ^{13}C T_1 data were obtained by the inversion recovery method¹⁷ on a GN500 spectrometer at 25°C .

Molecular modelling

We used the Chem-X program¹⁸ to model the structure of the complex based on minimization of the free energy. However, the predicted lengths of the Co—O(1A) and Co—O(2A) bonds are respectively longer and shorter by *ca* 0.4 Å than the crystallographic values probably because the program attempts to eliminate strain in the five-membered ring of the complex and does not consider effects of hydrogen bonding to water molecules.

Supplementary material for $\text{Co}(\text{NH}_3)_3(\text{L-malate})\cdot 2\text{H}_2\text{O}$. Table I, complete crystallographic data; Table II, atomic positions; Table III, anisotropic thermal parameters; Table IV, complete bond distances; Table V, complete bond angles; Table VI, hydrogen bonding interactions; Table VII, observed and calculated structure factors.

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