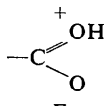


As in the first modification, the structure consists of dimeric units each consisting of crystallographically independent molecules *A* and *B*; however, unlike the first modification, the nitro groups of the dimer are in the *cis* configuration in this structure (Fig. 2). The dimers are loosely packed and this accounts for the lower density of these crystals (1.498 g cm^{-3}) in comparison with that of the crystals of the first modification (1.519 g cm^{-3}). The dimensions of *A* and *B* are not significantly different. The only difference between the molecular dimensions in the two crystal modifications is that the two C—O bonds of the carboxylic group in both *A* and *B* are nearly equal in the present structure [1.274 (8) and 1.278 (8) Å, and 1.279 (7) and 1.295 (7) Å], whereas they differ by about 0.04 Å in the first modification [1.260 (7) and 1.297 (8) Å, and 1.258 (8) and 1.298 (8) Å]. Apparently, there is less contribution from the structure



Acta Cryst. (1975). **B31**, 1980

The crystal structure of hydrated cobalt(II) 4-methyltropolonate. By M. L. POST* and J. TROTTER, *Department of Chemistry, University of British Columbia, Vancouver V6T 1W5, B.C., Canada*

(Received 26 February 1975; accepted 28 February 1975)

$P2_1/c$, $a = 10.147$ (5), $b = 25.492$ (8), $c = 20.135$ (8) Å, $\beta = 102.03$ (4)°; $Z = 4$ for $\text{C}_{48}\text{H}_{52}\text{O}_{17}\text{Co}_3$. The structure of cobalt(II) 4-methyltropolonate contains both a mononuclear and dinuclear species.

Tropolone, [TH], (Fig. 1, $R = \text{H}$) chelates many metal ions as a singly charged anionic ligand and forms oligomeric crystalline hydrates with Ni(II) and Co(II) (Post, 1971; Irving, Post & Povey, 1973; Irving, Post & Baker, 1975). The compact structure of the ligand (Shimanouchi & Sasada, 1973) is an important factor in the formation and stability of these two compounds. The Co(II) complex with 4-methyltropolone MeTH (Fig. 1, $R = \text{CH}_3$) has been the subject of an investigation into the effect caused by small-group substitutions in the tropolone ring upon the structural behaviour of the ligand. Present results indicate a reduction in packing efficiency.

Small, poorly formed crystals of hydrated Co(II) 4-methyltropolonate were grown from aqueous methanol. The space group was shown to be $P2_1/c$ and cell parameters, from 2θ values of diffractometer centred reflexions, are as given above. A crystal $0.05 \times 0.10 \times 0.08$ mm was mounted for diffractometer data collection with Zr-filtered Mo $K\alpha$ radiation and the θ - 2θ scan technique. 918 independent reflexions were measured which had $I \geq 3\sigma(I)$, and these were used in subsequent stages; the inherent resolution of the data was *ca* 1.4 Å. The quality and size of the crystal precluded collection of accurate data to yield a resolution better than this. The structure was solved by direct methods and, following successive full-matrix least-squares refine-

ment and difference syntheses, all the non-hydrogen atoms were placed. Convergence was attained at an R of 0.103† but the paucity of data and the large number of atoms in the asymmetric unit (68 non-hydrogen) caused poorly defined MeT skeletons in two of the ligands.

References

- DAVIES, E. S. & HARTSHORNE, N. H. (1934). *J. Chem. Soc.* pp. 1830–1836.
 DHANESHWAR, N. N., TAVALE, S. S. & PANT, L. M. (1974). *Acta Cryst.* **B30**, 583–587.
 LAI, T. F. & MARSH, R. E. (1967). *Acta Cryst.* **22**, 885–893.
 LONG, R. E. (1965). UCLA Dissertation, parts II & III.

† Tables of observed and calculated structure factors and of final atomic positional coordinates and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30960 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

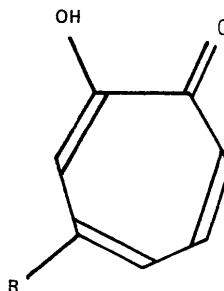


Fig. 1. Chemical diagram of tropolone ($R = \text{H}$) and 4-methyltropolone ($R = \text{CH}_3$).

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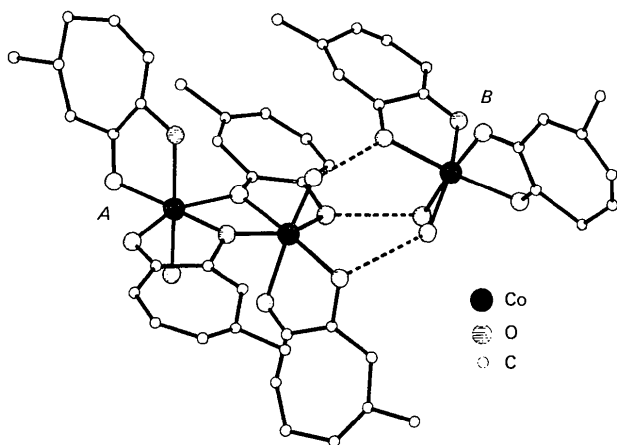


Fig. 2. A general view of the asymmetric unit of hydrated cobalt(II) 4-methyltropolonate (one non-bonded H_2O molecule omitted). Broken lines denote hydrogen bonds.

The asymmetric unit (Fig. 2) consists of a dimer (*A*) with formula $[\text{Co}(\text{MeT})_2\text{H}_2\text{O}]_2$, which has bridging MeT oxygen atoms and is structurally analogous to $[\text{NiT}_2\text{H}_2\text{O}]_2$, and a mononuclear species (*B*) with formula $\text{Co}(\text{MeT})_2(\text{H}_2\text{O})_2$ which exhibits *cis* configuration of water molecules. A non-bonded water molecule is also present. Hydrogen bonds exist between coordinated water molecules and ligand O

atoms; both H_2O molecules of *B* take part in this interaction but only one H_2O on *A* is involved, such that each *B* molecule is associated via three H-bonds (O—O distances 2.61, 2.73 and 2.75 Å) with one *A* molecule only. It is notable that there is no interaction between separate *A* pairs or *B* pairs, other than that induced by normal van der Waals approaches and that many of the shorter intermolecular contacts involve methyl C atoms.

Although the mother liquor must have contained both species, the relative concentration of each, and possibly others, in solution could have been a structure-determining factor for the solid state. However, the observed constitution of the stable lattice (the crystals were not moisture sensitive) would appear necessary to facilitate H-bonding and lattice packing which, because of the methyl substituent, is possibly not so efficiently achieved when either species is absent.

We thank the National Research Council of Canada for financial support.

References

- IRVING, R. J., POST, M. L. & BAKER, R. W. (1975). *J. Chem. Soc. Dalton*. In the press.
 IRVING, R. J., POST, M. L. & POVEY, D. C. (1973). *J. Chem. Soc. Dalton*, pp. 697–701.
 POST, M. L. (1971). Ph.D. Thesis, Univ. of Surrey.
 SHIMANOCHI, H. & SASADA, Y. (1973). *Acta Cryst. B* **29**, 81–90.

Acta Cryst. (1975). **B31**, 1981

Electron-density distribution in rutile crystals. By H. SHINTANI, S. SATO and Y. SAITO, *Institute for Solid State Physics, University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan*

(Received 10 February 1975; accepted 24 February 1975)

The distribution of residual electron density in rutile crystals has been calculated from intensities carefully obtained by diffractometry. There is no indication that the charge densities of Ti^{4+} (having no *d* electrons) are deformed in an octahedral crystal field. This result seems to support our conclusion that the aspherical charge densities of Ni^{2+} ($3d^8$) in $\gamma\text{-Ni}_2\text{SiO}_4$ are due to *d* electrons placed in an octahedral crystal field.

An indication of $3d$ electrons in the t_{2g} orbitals of Ni^{2+} and Co^{3+} was observed in the final difference syntheses of $\gamma\text{-Ni}_2\text{SiO}_4$ and $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ (Marumo, Isobe, Saito, Yagi & Akimoto, 1974; Iwata & Saito, 1973). In the difference maps eight small peaks were arranged at the corners of a cube around the transition metal atom, the peaks being at 0.45 Å from the metal atom. To see whether or not such peaks are due to *d* electrons, a difference synthesis of rutile, TiO_2 , was calculated based on carefully measured intensity data, since Ti^{4+} possesses no $3d$ electrons.

All attempts to shape a crystal specimen into a sphere failed. The specimen used had the dimensions $0.08 \times 0.08 \times 0.09$ mm. The intensities were collected on a Rigaku automated four-circle diffractometer. The experimental conditions were exactly the same as those for $\gamma\text{-Ni}_2\text{SiO}_4$,

Table 1. *Crystal data and atomic parameters*

$\text{TiO}_{2-\alpha}$, $\alpha = 0.016$ (7)	$U = 62.072 \text{ \AA}^3$ at 26°C
Tetragonal, $P4_2/mnm$	$D_m = 4.264 \text{ g cm}^{-3}$
$a = 4.5845$ (1) Å	$D_x = 4.260 \text{ g cm}^{-3}$
$c = 2.9533$ (1) Å	$Z = 2$

O at $(0, u, u)$ with $u = 0.30493$ (7)
 Isotropic extinction parameter $g = 0.29 \times 10^4$

The temperature factors are in the form:

$$\exp \{ -2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hka^* b^* U_{12} + 2hla^* c^* U_{13} + 2klb^* c^* U_{23}) \}$$

	$U_{11} = U_{22}$	U_{33}	U_{12}	U_{13}	U_{23}	($\times 10^5$)
Ti	699 (4)	467 (4)	-31 (9)	0	0	
O	601 (9)	454 (11)	-372 (22)	0	0	