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The Crystal and Molecular Structure of 1,10-Phenanthrolinebis(acetylacetonato)manganese(II)

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$C_{22}H_{22}N_2O_4Mn$ is orthorhombic, space group *Pbcn*, with $a = 15{\cdot}872 \pm 0{\cdot}032$, $b = 10{\cdot}279 \pm 0{\cdot}018$, $c = 12{\cdot}751 \pm 0{\cdot}020$ Å, $Z = 4$. The structure was refined to $R = 0{\cdot}068$ for 1097 visually estimated intensities. The molecule has space-group-imposed $2(C_2)$ symmetry. The coordination of the phenanthroline gives rise to a distorted octahedral environment about the Mn atom with Mn–O 2·152 (5) and 2·116 (5) Å and Mn–N 2·307 (5) Å. Both ligands are planar.

Introduction

Bis(acetylacetonato) complexes of first-row transition metals form 1:1 adducts with 1,10-phenanthroline and 2,2′-bipyridyl (Dwyer & Sargeson, 1956; Watton, Shadid, Stephens & Vagg, 1977). Since these bases can only coordinate *cis* to the metal atom, considerable distortion of the original coordination sphere must ensue. The reaction of diaquabis(acetylacetonato)-manganese(II) with either base results in the substitution of the *trans* water molecules by the base: either a distorted octahedral or trigonal-prismatic configuration may form. The structure of the 1,10-phenanthroline adduct is described here.

Experimental

The complex was prepared as orange crystals by adding 1,10-phenanthroline to an aqueous solution of Mn^{II} acetylacetonate.

Crystal data

$C_{22}H_{22}N_2O_4Mn$, $M_r = 433{\cdot}4$, orthorhombic, $a = 15{\cdot}872 \pm 0{\cdot}032$, $b = 10{\cdot}279 \pm 0{\cdot}018$, $c = 12{\cdot}751 \pm 0{\cdot}020$ Å, $U = 2080{\cdot}3$ Å^3, $D_m = 1{\cdot}38$ (by flotation), $Z = 4$, $D_c = 1{\cdot}383$ g cm^{-3}, $F(000) = 900$, μ(Mo $K\alpha$) = 6·7 cm^{-1}. Systematic absences $0kl$ if $k \neq 2n$, $h0l$ if $l \neq 2n$, $hk0$ if $h + k \neq 2n$, space group *Pbcn*.

Cell parameters were determined from precession photographs (Mo $K\alpha$ radiation). Intensities were estimated visually from precession photographs for the layers 0–5, 0–3 and 0–4 about **a**, **b** and [110] respectively. They were corrected for Lorentz and polarization effects but not for absorption or extinction. The structure factors were placed on a common scale by internal correlation, and 1097 non-zero unique reflexions were obtained.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on a Univac 1106 computer with programs written by the author.

Structure determination

The structure was solved by the heavy-atom method. Refinement was by full-matrix least squares in which $\Sigma\, w\Delta^2$ was minimized. Weights were initially unity but

Table 1. *Final atomic coordinates* (*fractional*, $\times 10^4$ *for nonhydrogen atoms*, $\times 10^3$ *for* H *atoms*) *with estimated standard deviations in parentheses*

	x	y	z
Mn	0	284 (1)	2500
O(11)	1210 (3)	224 (5)	1739 (3)
O(12)	607 (3)	1580 (5)	3545 (4)
N	340 (3)	−1525 (5)	3484 (4)
C(11)	1914 (5)	496 (7)	2169 (6)
C(12)	2028 (5)	1190 (8)	3076 (6)
C(13)	1380 (5)	1706 (7)	3712 (6)
C(111)	2680 (5)	−22 (11)	1576 (8)
C(131)	1629 (6)	2471 (9)	4668 (9)
C(1)	677 (5)	−1521 (7)	4422 (5)
C(2)	890 (4)	−2659 (7)	4973 (5)
C(3)	729 (5)	−3839 (7)	4504 (5)
C(4)	373 (4)	−3899 (6)	3509 (5)
C(5)	192 (4)	−2701 (6)	3021 (4)
C(6)	182 (4)	−5089 (6)	2978 (5)
H(111)	273	−73	192
H(112)	314	57	184
H(113)	257	7	80
H(131)	129	211	527
H(132)	124	323	481
H(133)	216	259	474
H(12)	266	199	337
H(1)	78	−67	478
H(2)	107	−258	569
H(3)	87	−463	492
H(6)	25	−598	334

in the final stages $w = (25{\cdot}0 + |F_o| + 0{\cdot}07|F_o|^2)^{-1}$ was used. Reflexions for which $|F_c| < 0{\cdot}333|F_o|$ were omitted.

After refinement in which positional and individual isotropic thermal parameters were varied, a difference synthesis yielded the positions of all H atoms which were included with a thermal parameter of $B = 6{\cdot}0$ Å^2, but not refined. Final refinement was with anisotropic thermal parameters for all nonhydrogen atoms, and was terminated when the maximum shift in any parameter was $<0{\cdot}05\sigma$. 1095 reflexions were included in the final cycle. The final R, based on 1097 reflexions, was 0·068 and R' $[=(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}]$ was 0·089. A final difference map showed no features $>|0{\cdot}9|$ e Å^{-3} and these were associated with the Mn atom. The final atomic coordinates are given in Table 1.*

Discussion

The geometry of the complex and the labelling of the atoms are shown in Fig. 1. Fig. 2 shows the packing of the molecules. The molecules are held in the crystal by van der Waals forces. The closest intermolecular contacts are O(12)···C(2)[$-x$, $-y$, $1-z$] 3·23, O(12)···C(1)[$-x$, $-y$, $1-z$] 3·30, O(11)···C(1)[x, $-y$, $z-\frac{1}{2}$] 3·34 and O(11)···C(2)[x, $-y$, $z-\frac{1}{2}$] 3·40 Å. All other nonhydrogen contacts are $>3{\cdot}5$ Å.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32742 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

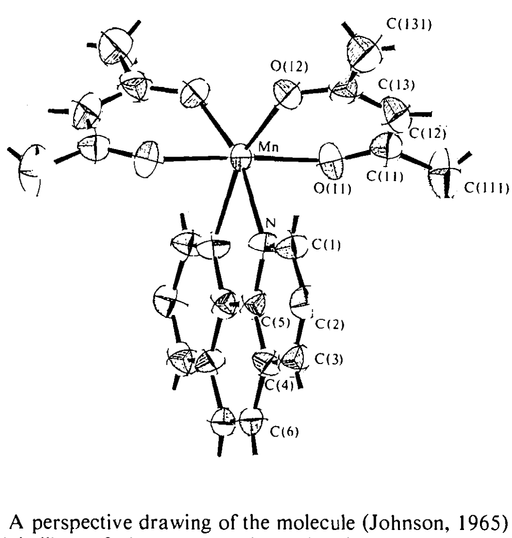

Fig. 1. A perspective drawing of the molecule (Johnson, 1965) and the labelling of the atoms. Thermal ellipsoids are scaled to include 35% probability.

The bond distances and angles are given in Table 2. The complex has space-group-imposed $2(C_2)$ symmetry. The environment about the Mn atom is a distorted octahedron and closely parallels that observed in the 1,10-phenanthroline adduct of bis(difluoroborondiphenylglyoximato)nickel(II) (Stephens & Vagg, 1977); both have the imposed symmetry $2(C_2)$, and the angles between the ligand-atom planes are comparable (acac/acac 76·1, glyoxime/glyoxime 75·7 and acac/phen 62·6, glyoxime/phen 65·1°).

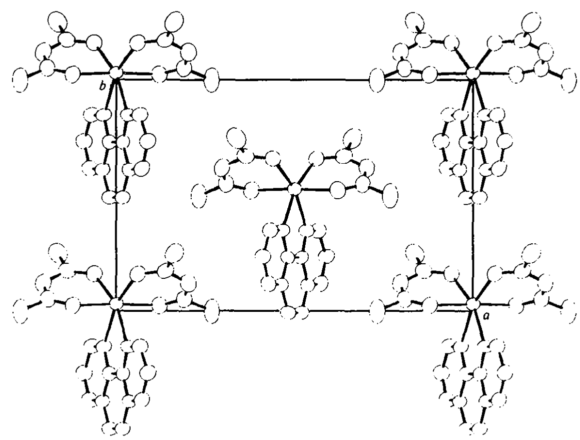

Fig. 2. The packing of the molecules in the crystal.

Table 2. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

Atoms marked with a prime are related to those at (x,y,z) by the twofold axis at $(0,y,\frac{1}{4})$.

Mn–O(11)	2·152 (5)	N–C(1)	1·311 (8)
Mn–O(12)	2·116 (5)	N–C(5)	1·366 (8)
Mn–N	2·307 (5)	C(1)–C(2)	1·406 (9)
O(11)–C(11)	1·276 (8)	C(2)–C(3)	1·376 (9)
O(12)–C(13)	1·251 (8)	C(3)–C(4)	1·390 (9)
C(11)–C(12)	1·371 (10)	C(4)–C(5)	1·409 (8)
C(12)–C(13)	1·414 (11)	C(4)–C(6)	1·431 (9)
C(11)–C(111)	1·529 (11)	C(5)–C(5′)	1·461 (11)
C(13)–C(131)	1·505 (11)	C(6)–C(6′)	1·348 (12)

O(11)–Mn–O(12)	84·0 (2)	Mn–O(11)–C(11)	125·5 (4)
N–Mn–N′	72·6 (2)	Mn–O(12)–C(13)	128·2 (5)
O(11)–Mn–O(11′)	176·7 (2)	O(11)–C(11)–C(12)	126·4 (7)
N–Mn–O(12′)	163·0 (2)	O(11)–C(11)–C(111)	114·1 (7)
O(11)–Mn–O(12′)	98·1 (2)	C(12)–C(11)–C(111)	119·6 (7)
O(11)–Mn–N	90·8 (2)	O(12)–C(13)–C(12)	125·2 (7)
O(11)–Mn–N′	86·6 (2)	O(12)–C13)–C(131)	116·8 (7)
O(12)–Mn–O(12′)	102·0 (2)	C(12)–C(13)–C(131)	118·0 (7)
O(12)–Mn–N	93·4 (2)	C(11)–C(12)–C(13)	125·6 (7)
Mn–N–C(1)	126·1 (4)	C(3)–C(4)–C(6)	123·8 (6)
Mn–N–C(5)	116·0 (4)	C(5)–C(4)–C(6)	119·6 (5)
C(1)–N–C(5)	117·9 (5)	C(4)–C(5)–N	123·2 (5)
N–C(1)–C(2)	123·5 (6)	C(4)–C(5)–C(5′)	117·7 (5)
C(1)–C(2)–C(3)	118·2 (5)	C(5′)–C(5)–N	119·1 (4)
C(2)–C(3)–C(4)	120·7 (6)	C(4)–C(6)–C(6′)	121·2 (6)
C(3)–C(4)–C(5)	116·6 (6)		

Table 3. *Least-squares planes and their equations given by $lX + mY + nZ - p = 0$, where X,Y,Z are atomic coordinates in* Å

Deviations (Å) of the most relevant atoms from the planes are given in square brackets.

	l	m	n	p
Plane 1: O(11), O(12), C(11), C(12), C(13)	−0·0196	−0·8546	0·5188	0·9267
[O(11), C(13) −0·01; O(12), C(11) 0·01; C(12) 0·001; C(111) 0·05; C(131) −0·06; Mn 0·48]				
Plane 2: C(11), O(11), C(12), C(111)	−0·0447	−0·8482	0·5279	0·8897
[C(11) 0·002; O(11), C(12), C(111) −0·0006]				
Plane 3: C(13), O(12), C(12), C(131)	−0·0055	−0·8397	0·5430	1·0851
[C(13) 0·0005; O(12), C(12), C(131) −0·0002]				
Plane 4: N, C(1)–C(6)	−0·9125	−0·0105	0·4089	1·3354
[N 0·005; C(1) 0·006; C(2) −0·003; C(3) −0·001; C(4) −0·004; C(5) −0·010; C(6) 0·008; Mn −0·04]				

Table 4. *Dimensions (in* Å *and degrees) in acetylacetonatomanganese*(II) *complexes*

	$Mn(acac)_2(H_2O)_2$		$[(Allylamine)Mn(acac)_2]_2$	$Mn(acac)_2(phen)$
	(*a*)	(*b*)	(*c*)	(*d*)
Mn–O	2·142 (8)	2·150 (8)	2·14 (2)	2·152 (5)
	2·123 (8)	2·128 (8)	2·31 (2)†	2·116 (5)
Mn–*L**	2·257 (8)	2·267 (8)	2·31 (2)	2·307 (5)
C–O	1·29	1·29	1·29	1·26
C–C	1·40	1·42	1·40	1·39
C–Me	1·50	1·51	1·53	1·52
O–Mn–O	85·9 (3)	86·2	‡	84·0 (2)
Mn–O–C	124	125	‡	127
O–C–C	125	125	‡	126
O C–Me	116	116	‡	115
C–C–Me	119	120	‡	119
C–C–C	127	128	‡	126

(*a*) Montgomery & Lingafelter (1968). (*b*) Onuma & Shibata (1970). (*c*) Koda, Ooi & Kuroya (1972). (*d*) Present work.

* *L* is the ligand atom completing octahedral coordination.
† Distance for Mn to bridging O atom.
‡ Data not given.

The two ligands are planar (planes 1 and 4, Table 3) but the Mn atom lies 0·5 Å from the acac plane. C(11) and C(13) of acac are both trigonally planar (planes 2 and 3, Table 3) and the bond lengths indicate that the double bond is delocalized over the backbone of the ligand.

The average dimensions within the Mn(acac) fragment are compared in Table 4 with those from other acetylacetonatomanganese(II) structures. The Mn–O(acac) distances in $[Mn(acac)_2(H_2O)_2]$ (Montgomery & Lingafelter, 1968; Onuma & Shibata, 1970) are not equal but their difference is not significant. In the present complex the difference is significant, $\Delta L/\sigma(\Delta L) = 5{\cdot}1$ (Jeffrey & Cruickshank, 1953). The reason for this is not evident. The Mn–N distance (2·307 Å) is similar to the 2·31 Å in $[(allylamine)\text{-}Mn(acac)_2]_2$ (Koda, Ooi & Kuroya, 1972) and the 2·324 Å to the pyridine ring in $[Mn(NC_5H_4\text{-}CONC_2H_5)_2(NCS)_2]$ (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1973).

References

BIGOLI, F., BRAIBANTI, A., PELLINGHELLI, M. A. & TIRIPICCHIO, A. (1973). *Acta Cryst.* B**29**, 39–43.

DWYER, F. P. & SARGESON, M. A. (1956). *J. Proc. Roy. Soc. NSW*, **90**, 29–33.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–77. Birmingham: Kynoch Press.

JEFFREY, G. A. & CRUICKSHANK, D. W. J. (1953). *Quart. Rev.* **4**, 335–376.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, revised 1971. Oak Ridge National Laboratory, Tennessee.
KODA, S., OOI, S. & KUROYA, H. (1972). *Inorg. Nucl. Chem. Lett.* **8**, 89–92.
MONTGOMERY, H. & LINGAFELTER, E. C. (1968). *Acta Cryst.* B**24**, 1127–1128.
ONUMA, S. & SHIBATA, S. (1970). *Bull. Chem. Soc. Japan*, **43**, 2395–2397.
STEPHENS, F. S. & VAGG, R. S. (1977). *Acta Cryst.* B**33**, 3165–3169.
WATTON, E. C., SHADID, F. R., STEPHENS, F. S. & VAGG, R. S. (1977). Unpublished results.

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Crystal Structure of Ferroelectric Guanidinium Uranyl Sulphate Trihydrate

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The crystal structure of the ferroelectric title compound has been determined from three-dimensional X-ray data, and refined by full-matrix least-squares calculations to an R value of 6·9%. Although physical evidence required a non-centrosymmetric space group, convergence could only be achieved in the centrosymmetric monoclinic space group $C2/c$. The U coordination polyhedron is a pentagonal bipyramid with the uranyl O atoms at the apices. Sulphate groups, acting as bridging ligands, join polyhedra together to form a tightly bound two-dimensional network parallel to (001). A fairly complex H bonding pattern holds layers together, *via* the guanidinium groups and the water of crystallization. [Crystal data: $a = 11·220$ (8), $b = 8·027$ (4), $c = 18·681$ (8) Å, $\beta = 101°$ (4′), $U = 1652$ (1) Å^3.]

Introduction

As part of a general study of the relationship between crystal structure and electrical properties of uranyl compounds, we report here the crystal and molecular structure of guanidinium uranyl sulphate trihydrate (hereinafter GUSH), as obtained from three-dimensional X-ray photographic data.

Interest in this study was stimulated by the fact that the material has been found to be ferroelectric (de Benyacar, de Dussel & de Wainer, 1977).

Experimental

The material used throughout this investigation was synthetized following Canneri (1925). After recrystallization from a saturated water solution at room temperature, well developed thick plates were obtained which, under optical investigation, showed a biaxial interference figure corresponding to an orthorhombic, or lower, symmetry (X-ray diffraction patterns showed later that the true lattice symmetry was monoclinic).

A crystal suitable for X-ray analysis was mounted along **b**, and $hk0$ and $0kl$ precession photographs were taken with Mo $K\alpha$ radiation, from which accurate cell dimensions were measured and later confirmed by the least-squares fit of a calibrated powder diagram (Table 1).

Table 1. *Indexed powder diagram of GUSH*

$h\,k\,l$	d_{obs} (Å)	d_{cal} (Å)
0 0 2	9·158	9·169
1 1 1	6·349	6·344
1 1 1	5·912	5·910
2 0 2	5·177	5·177
1 1 2	5·038	5·036
1 1 3	4·723	4·721
0 0 4	4·584	4·585
2 0 2	4·368	4·368
1 1 3	4·220	4·219
0 2 1	3·916	3·921
0 2 2	3·678	3·677
1 1 4	3·560	3·560
3 1 1	3·389	3·390
1 1 5	3·357	3·358
0 2 3		3·355
2 2 0	3·245	3·243
2 2 2	3·172	3·172
3 1 3		3·171
0 0 6	3·054	3·056
2 2 2	2·955	2·955
3 1 4		2·954
2 0 6	2·919	2·919
1 3 2	2·529	2·531
1 1 7		2·530
0 0 8	2·293	2·292
4 0 6	2·273	2·273
4 2 0		2·270