

Contribution from the Department of Chemistry,
Case Western Reserve University, Cleveland, Ohio 44106**Crystal and Molecular Structure of Tris(2,4-pentanedionato)manganese(III), $Mn(O_2C_5H_7)_3$, a Distorted Complex As Predicted by Jahn-Teller Arguments**

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The crystal and molecular structure of manganese(III) acetylacetonate, $Mn(acac)_3$, has been determined by three-dimensional X-ray analysis. The compound crystallizes in the monoclinic space group $C_{2h}^5-P2_1/c$ (No. 14) with $a = 14.013$ (1) Å, $b = 7.600$ (1) Å, $c = 16.373$ (1) Å, and $\beta = 99.33$ (1)°. Least-squares refinement of 1771 reflections resulted in a final conventional R factor of 0.084. It is suggested that the previously reported structure of $Mn(acac)_3$ [B. Morosin and J. R. Brathovde, *Acta Crystallogr.*, 17, 705 (1964)] is actually the structure of $Co(acac)_3$. The $Mn(acac)_3$ molecule in the crystal we have studied is tetragonally distorted. The two average Mn-O bond distances are 1.95 and 2.00 Å in a compressed MnO_6 octahedron. The O ··· O "bite" distance measures 2.79 Å. Comparison with the structures of other tris(acetylacetonates) shows that the molecule has no appreciable trigonal distortion. A crystal field calculation is presented in an attempt to understand the Jahn-Teller distortions observed.

Introduction

The short Mn-O bond distances and the lack of the anticipated tetragonal distortion in the reported structure of tris(acetylacetonato)manganese(III), $Mn(acac)_3$, by Morosin and Brathovde¹ (MB) has been intriguing and puzzling.²⁻⁶ Of the few other "octahedral" molecular Mn(III) complexes whose structures have been reported,^{3,5-8} all show tetragonal distortion attributable to the operation of Jahn-Teller⁹ forces. The tetragonal MnO_6 geometries found for tris(tropolonato)manganese(III),^{5,6} $Mn(trop)_3$, cast doubt upon the MB result.

Lingafelter¹⁰ recently reexamined the cell parameters of most of the first-row transition metal-tris(acetylacetonate) complexes and found some discrepancy with those reported for $Mn(acac)_3$ by MB. It appeared, on the other hand, that the cell parameters reported by MB did correspond very closely to those of $Co(acac)_3$. Pfluger¹¹ initially pointed out¹² the similarity between the cobalt and the MB structure.

Since the possibility was strong that the $Mn(acac)_3$ and $Co(acac)_3$ compounds were mislabeled and that the MB structure was actually that of $Co(acac)_3$,¹² it was decided that the structure of $Mn(acac)_3$ should be redetermined. A preliminary account of the results has been reported.¹³

Experimental Section

Space Group and Lattice Parameters. Examination of a sample of $Mn(acac)_3$ crystals prepared in our group some 10 years ago revealed isomorphism with the reported iron,¹⁴ scandium,¹⁵ and α -

vanadium¹⁶ structures, which have an orthorhombic space group, $Pbca$. This sample was labeled α - $Mn(acac)_3$ by analogy with the α,β dimorphism (orthorhombic, monoclinic) also observed for $V(acac)_3$.¹⁶ The monoclinic β - $Mn(acac)_3$ complex, the structure of which is reported here, was prepared by a well-established literature procedure.¹⁷ The lustrous dark brown crystals, once recrystallized from benzene-ether, were found to be suitable for intensity data collection as evidenced from preliminary film examinations of several crystals of varied shapes and sizes. The common habit was that of a slightly distorted hexagonal prism (0.2-2.0 mm in size) bounded by 001, 100, 110, and $1\bar{1}0$ faces. From precession X-ray film examinations of a cut crystal, the systematic extinctions were consistent with the space group $C_{2h}^5-P2_1/c$ (No. 14). The lattice parameters were deduced (at ambient room temperature) from the angular settings of 16 carefully centered reflections, average $2\theta = 41^\circ$ (Mo $K\alpha$ radiation), 1° takeoff angle, on the Picker card-controlled four-circle automatic diffractometer (Table I).

Collection and Reduction of Intensity Data. Initial attempts to collect data with copper radiation failed when the crystal decomposed with an approximate half-life of 24 hr. Using molybdenum radiation with a fresh crystal some deterioration was observed, possibly attributable to surface decomposition. Relatively more decomposition occurred using smaller crystals, and decomposition leveled off for large crystals after the initial 1500 reflections at 80% of the initial standard intensity with no further deterioration for the subsequent 1500 reflections.

With the above information in mind the final data collection was planned to be as rapid as possible with minimal sacrifice to accuracy. A relatively large crystal was chosen (see Table I). It was mounted and coated with Elmer's white glue (dries transparent). Precautions were taken to ensure that the crystal was always inside the X-ray beam, the outlines of which could be observed visually. Zirconium-filtered Mo $K\alpha$ radiation ($\lambda_{K\alpha} = 0.7107$ Å) was used. The crystal was mounted such that the c^* axis was collinear with the ϕ axis of the diffractometer. The pulse height analyzer was set to admit about 95% of the Mo $K\alpha$ radiation, using the relatively intense reflection 302. The θ - 2θ scan mode was used with 8-sec preset stationary-background counting times at the high and low limits of the scan, 1.5° takeoff angle, and the X-ray generator set at 40 kV and 18 mA.

At $\chi = 90^\circ$ the slow scan in ϕ for the (0,0,10) reflection ($2\theta = 25.3^\circ$) showed a maximum variation of $\pm 5\%$ in the intensity. With the average μ_r value perpendicular to the χ plane being 0.55 it was decided that no absorption corrections would be performed on the data. The added intensity gained from a large crystal was advantageous in this case. The crystal data are summarized in Table I.

Scan ranges varying from 0.9 to 1.4° for the intensity data collection were chosen on the basis of the crystal mosaicity and the source size. Many reflections were monitored with a chart recorder at various stages of the data collection to ensure that centering was proper.

Consistent with the suspicion that the previously observed decomposition was of surface nature, the coated crystal showed essentially no deterioration during the entire data collection. Only

(1) B. Morosin and J. R. Brathovde, *Acta Crystallogr.*, 17, 705 (1964).

(2) T. S. Davis, J. P. Fackler, Jr., and M. J. Weeks, *Inorg. Chem.*, 7, 1994 (1968).

(3) M. Bartlett and G. J. Palenik, *J. Chem. Soc. D*, 416 (1970).

(4) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, p 851.

(5) J. P. Fackler, Jr., A. Avdeef, and J. Costamagna, *Proc. Int. Conf. Coord. Chem.*, 14, 589 (1972).

(6) A. Avdeef, J. A. Costamagna, and J. P. Fackler, Jr., *Inorg. Chem.*, 13, 1854 (1974).

(7) K. Knox, *Acta Crystallogr.*, 16, 1445 (1963).

(8) P. C. Healey and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1883 (1972).

(9) H. A. Jahn and E. Teller, *Proc. Roy. Soc., London*, 161, 200 (1937); H. A. Jahn, *ibid.*, 164, 117 (1938).

(10) E. C. Lingafelter, private communication, June 1972.

(11) C. E. Pfluger, private communication to B. Morosin, 1964.

(12) B. Morosin, private communication, Dec 1972.

(13) J. P. Fackler, Jr., and A. Avdeef, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973, No. INOR 64.

(14) J. Iball and C. H. Morgan, *Acta Crystallogr.*, 23, 239 (1967).

(15) T. J. Anderson, M. A. Neuman, and G. A. Melson, *Inorg. Chem.*, 12, 927 (1973).

(16) B. Morosin and H. Montgomery, *Acta Crystallogr., Sect. B*, 25, 1354 (1969).

(17) R. G. Charles and B. E. Bryant, *Inorg. Syn.*, 7, 183 (1966).

Table I. Summary of Crystal Data for Mn(acac) (Monoclinic)

| | |
|---|--|
| Molecular formula | Mn(O ₂ C ₅ H ₇) ₃ |
| FW | 352.27 |
| d_{calcd} , g/cm ³ | 1.368 |
| d_{obsd} , g/cm ³ | 1.34 (5) |
| Z, formula units/cell | 4 |
| Linear absorption coeff, μ , cm ⁻¹ | 8.36 |
| λ (Mo K α), Å | 0.7107 |
| Crystal dimensions ^a | 0.365 mm thick (c^*), 0.55–0.75 mm diameter (ab plane) |
| Systematic absences | $h0l, l = 2n + 1$ $0k0, k = 2n + 1$ |
| Space group | $C_{2h}^5-P2_1/c$ (No. 14) |
| Cell constants ^b | |
| a , Å | 14.013 (1) |
| b , Å | 7.600 (1) |
| c , Å | 16.373 (1) |
| β , deg | 99.33 (1) |
| $\cos \beta$ | -0.162086 |
| U , Å ³ | 1720.6 |
| $F(000)$ | 684 |

^a Cut to approximately disk shape. ^b At 22 (2)^o; least-squares fit; 16 reflections; $2\theta_{\text{av}} = 41^\circ$ for Mo K α ; peak of the resolved doublet; λ 0.70926 Å.

one standard reflection, $80\bar{8}$, was monitored approximately every 100 reflections. Using three general standards with the earlier data collection attempts, decomposition had been found to be essentially isotropic. The final coated crystal showed only a nominal linear decomposition amounting to a drop in intensity of about $1/2\sigma$ ($I_{\text{std}}/3000$ reflections). To account for this the data were scaled to the results of a linear least-squares fit of the intensities of the standards [scale factor = $C_o/(C_o - 0.0128n)$; $C_o = 3913$ decacounts, the interpolated initial intensity of the standard; n is the total number of reflections collected up to the time a particular standard was measured]. A $\pm 2\%$ maximum fluctuation in the standards was observed.

The definitions of intensities and associated errors used here have been defined.¹⁸ The electronic instability constant p was set at 2%. The intensity data collection was carried out for one quadrant of reciprocal space to a maximum ($\sin \theta$)/ λ of 0.595 ($2\theta \approx 50^\circ$), encompassing 2969 nonsystematically absent reflections of which 2447 had intensities larger than one standard deviation. The 1774 data used for refinement of the structure consisted of the set where $I/\sigma(I)$ was 3 or larger. The data reduction process incorporated the usual¹⁸ Lorentz and polarization corrections.

Solution and Refinement of the Structure. The solution of the structure proved to be quite simple. Using MB's atomic coordinates the calculated discrepancy factors¹⁹ were $R = 0.40$ and $R_w = 0.48$. Six isotropic full-matrix least-squares²⁰ cycles brought the factors down to 0.152 and 0.164, respectively, using unit weights. Two more isotropic and two more anisotropic least-squares cycles, with a Cruickshank type weighting scheme, brought the discrepancy factors down to 0.098 and 0.146. It was noted that the three highest intensity structure factors 002, 200, and 110 were consistently some 30 electrons lower than the calculated ones. These same reflections were observed to suffer from secondary extinctions in the Cr(acac)₃,²¹ Al(acac)₃,²² and Co(acac)₃²² structures. These three reflections were deleted from the data set used in further refinement.

The atomic scattering factors for neutral atoms were taken from Cromer and Waber²³ and from Stewart, *et al.*²⁴ Anomalous dispersion corrections²⁵ (real and imaginary) were incorporated for the manganese scattering factors.

Two more anisotropic least-squares cycles yielded $R = 0.086$ and $R_w = 0.122$. At this point the refinement of the hydrogen-excluded structure converged.

(18) J. P. Fackler, Jr., A. Avdeef, and R. G. Fischer, Jr., *J. Amer. Chem. Soc.*, **95**, 774 (1973).

(19) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2] / \sum w|F_o|^2$. $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively.

(20) The function minimized is $\sum w(|F_o| - |F_c|)^2$.

(21) B. Morosin, *Acta Crystallogr.*, **19**, 131 (1965).

(22) P. K. Hon and C. E. Pfluger, *J. Coord. Chem.*, **3**, 67 (1973).

A preprint of this article was kindly sent to us by Dr. Pfluger.

(23) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(24) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(25) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

Table II. Summary of Final Refinement Characteristics for Mn(acac)₃

| | |
|---|---------------------------------------|
| Data used | $I/\sigma(I) \geq 3.0$ |
| No. of reflections (not corrected for absorption) | 1771 |
| No. of varied parameters (nonhydrogen)/cycle | 199 |
| No. of reflections/no. of varied parameters | 8.9 |
| Final R | 0.084 |
| Final R_w | 0.118 |
| Final Erf | 1.36 |
| Final weighting scheme, Cruickshank type | $w_i = (\Delta F_i)^{-2}$ |
| ΔF (reduced $\chi^2 = 2.26$) | $1.2606 + 0.00820F_o + 0.000279F_o^2$ |
| Max. position shift/error (nonhydrogen) | $0.10[z \text{ of C}(2)]^a$ |
| Max. thermal shift/error (nonhydrogen) | $0.15[\beta_{22} \text{ of C}(1-2)]$ |

^a 0.002-Å atomic shift.

Table III. Positional Parameters and Estimated Standard Deviations of Mn(acac)₃

| | x | y | z |
|--------|--------------|--------------|-------------|
| Mn | 0.2354 (1) | 0.2638 (2) | 0.4725 (1) |
| O(1) | 0.1105 (8) | 0.3325 (12) | 0.4132 (5) |
| O(2) | 0.1742 (5) | 0.1876 (11) | 0.5682 (4) |
| O(3) | 0.3635 (5) | 0.1931 (9) | 0.5288 (4) |
| O(4) | 0.2952 (6) | 0.3365 (9) | 0.3759 (4) |
| O(5) | 0.2161 (5) | 0.0198 (10) | 0.4237 (4) |
| O(6) | 0.2568 (6) | 0.5033 (10) | 0.5232 (4) |
| C(1) | 0.0313 (13) | 0.3194 (34) | 0.4365 (10) |
| C(2) | 0.0863 (9) | 0.1827 (32) | 0.5724 (8) |
| C(3) | 0.4298 (8) | 0.2914 (16) | 0.5634 (7) |
| C(4) | 0.3007 (7) | 0.2470 (15) | 0.3115 (6) |
| C(5) | 0.2343 (7) | -0.0291 (13) | 0.3542 (6) |
| C(6) | 0.3351 (11) | 0.5634 (15) | 0.5620 (6) |
| C(1-2) | 0.0146 (12) | 0.2473 (44) | 0.5079 (10) |
| C(4-5) | 0.2732 (7) | 0.0714 (15) | 0.2990 (6) |
| C(3-6) | 0.4217 (9) | 0.4707 (17) | 0.5806 (7) |
| C(1M) | -0.0563 (16) | 0.3737 (46) | 0.3684 (11) |
| C(2M) | 0.0637 (14) | 0.1156 (46) | 0.6549 (11) |
| C(3M) | 0.5281 (8) | 0.2017 (20) | 0.5932 (9) |
| C(4M) | 0.3442 (9) | 0.3458 (17) | 0.2455 (6) |
| C(5M) | 0.2101 (9) | -0.2228 (15) | 0.3327 (7) |
| C(6M) | 0.3297 (13) | 0.7581 (16) | 0.5890 (8) |
| H1M1 | -0.032 | 0.410 | 0.317 |
| H1M2 | -0.101 | 0.271 | 0.356 |
| H1M3 | -0.092 | 0.474 | 0.389 |
| H12 | -0.054 | 0.246 | 0.518 |
| H2M1 | 0.126 | 0.086 | 0.692 |
| H2M2 | 0.022 | 0.007 | 0.645 |
| H2M3 | 0.028 | 0.209 | 0.681 |
| H4M1 | 0.391 (9) | 0.409 (19) | 0.265 (8) |
| H4M2 | 0.393 (10) | 0.205 (22) | 0.253 (9) |
| H4M3 | 0.303 (10) | 0.365 (19) | 0.203 (9) |
| H45 | 0.265 (10) | 0.036 (21) | 0.242 (9) |
| H5M1 | 0.209 (11) | -0.294 (19) | 0.382 (9) |
| H5M2 | 0.252 (11) | -0.266 (21) | 0.285 (9) |
| H5M3 | 0.132 (7) | -0.231 (13) | 0.299 (6) |
| H3M1 | 0.523 | 0.073 | 0.579 |
| H3M2 | 0.579 | 0.257 | 0.565 |
| H3M3 | 0.548 | 0.217 | 0.654 |
| H36 | 0.480 | 0.535 | 0.609 |
| H6M1 | 0.263 | 0.804 | 0.571 |
| H6M2 | 0.377 | 0.830 | 0.563 |
| H6M3 | 0.346 | 0.766 | 0.651 |

A difference Fourier synthesis showed all the hydrogen atoms associated with the O(4)-O(5) acac plane but the other hydrogen atoms could not be unambiguously located. Those atoms which were located were varied²⁶ isotropically and in position while the rest of the hydrogen atoms were included at calculated positions with B set to 10 Å², assuming an sp^3 angle for the methyl hydrogens and an angle for the methylene hydrogens such that they were

(26) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

Table IV. Thermal Parameters^a and Estimated Standard Deviations for Mn(acac)

| | β_{11} or B , Å ² | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|--------|--------------------------------------|--------------|--------------|--------------|--------------|--------------|
| Mn | 0.0081 (1) | 0.0227 (3) | 0.0039 (1) | 0.0035 (1) | 0.0015 (1) | -0.0000 (1) |
| O(1) | 0.0131 (8) | 0.0406 (24) | 0.0058 (4) | 0.0101 (11) | -0.0008 (4) | -0.0016 (7) |
| O(2) | 0.0065 (4) | 0.0435 (22) | 0.0051 (3) | 0.0010 (7) | 0.0012 (3) | 0.0014 (7) |
| O(3) | 0.0070 (4) | 0.0254 (15) | 0.0056 (3) | 0.00125 (7) | 0.0011 (3) | -0.0001 (5) |
| O(4) | 0.0163 (8) | 0.0249 (15) | 0.0041 (3) | -0.0002 (9) | 0.0031 (4) | -0.0018 (5) |
| O(5) | 0.0102 (6) | 0.0294 (17) | 0.0052 (3) | 0.0017 (8) | 0.0024 (3) | 0.0001 (6) |
| O(6) | 0.0117 (7) | 0.0287 (17) | 0.0049 (3) | 0.0054 (9) | 0.0013 (4) | -0.0006 (6) |
| C(1) | 0.0101 (12) | 0.1172 (101) | 0.0069 (8) | 0.0215 (28) | -0.0030 (8) | -0.0086 (23) |
| C(2) | 0.0062 (8) | 0.1258 (97) | 0.0057 (6) | -0.0031 (23) | 0.0017 (5) | -0.0000 (21) |
| C(3) | 0.0080 (8) | 0.0302 (27) | 0.0057 (5) | -0.0005 (12) | 0.0032 (5) | 0.0016 (9) |
| C(4) | 0.0063 (5) | 0.0314 (25) | 0.0042 (3) | 0.0032 (11) | 0.0006 (4) | 0.0004 (9) |
| C(5) | 0.0057 (6) | 0.0257 (22) | 0.0047 (5) | 0.0019 (9) | -0.0008 (4) | -0.0004 (8) |
| C(6) | 0.0149 (12) | 0.0242 (24) | 0.0033 (4) | -0.0000 (14) | 0.0024 (6) | 0.0006 (8) |
| C(1-2) | 0.0092 (11) | 0.1871 (149) | 0.0049 (6) | 0.0195 (34) | -0.0002 (7) | -0.0024 (28) |
| C(4-5) | 0.0069 (7) | 0.0267 (24) | 0.0044 (4) | 0.0002 (10) | 0.0001 (4) | -0.0021 (8) |
| C(3-6) | 0.0103 (9) | 0.0293 (29) | 0.0063 (6) | -0.0005 (13) | 0.0016 (6) | 0.0007 (10) |
| C(1M) | 0.0201 (20) | 0.1880 (169) | 0.0080 (9) | 0.0478 (52) | -0.0055 (11) | -0.0100 (33) |
| C(2M) | 0.0138 (15) | 0.1897 (166) | 0.0073 (8) | -0.0282 (43) | 0.0038 (9) | -0.0027 (33) |
| C(3M) | 0.0062 (7) | 0.0487 (42) | 0.0108 (9) | 0.0041 (14) | 0.0015 (6) | 0.0022 (15) |
| C(4M) | 0.0120 (10) | 0.0357 (30) | 0.0044 (5) | -0.0025 (14) | 0.0021 (5) | 0.0012 (9) |
| C(5M) | 0.0100 (8) | 0.0263 (26) | 0.0074 (6) | -0.0030 (12) | -0.0006 (6) | -0.0010 (10) |
| C(6M) | 0.0247 (19) | 0.0198 (23) | 0.0067 (6) | 0.0020 (17) | 0.0034 (9) | -0.0017 (10) |
| H4M1 | 11.1 (37) | | | | | |
| H4M2 | 19.3 (46) | | | | | |
| H4M3 | 18.8 (41) | | | | | |
| H45 | 17.5 (45) | | | | | |
| H5M1 | 17.2 (44) | | | | | |
| H5M2 | 16.8 (47) | | | | | |
| H5M3 | 8.4 (26) | | | | | |

^a The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table V. Root-Mean-Square Displacement of Thermal Ellipsoids (in Å) for Mn(acac)₃

| | | | |
|--------|-------|-------|-------|
| Mn | 0.213 | 0.238 | 0.303 |
| O(1) | 0.253 | 0.280 | 0.433 |
| O(2) | 0.246 | 0.259 | 0.357 |
| O(3) | 0.251 | 0.273 | 0.280 |
| O(4) | 0.207 | 0.277 | 0.397 |
| O(5) | 0.247 | 0.288 | 0.324 |
| O(6) | 0.245 | 0.265 | 0.363 |
| C(1) | 0.207 | 0.306 | 0.638 |
| C(2) | 0.232 | 0.278 | 0.608 |
| C(3) | 0.217 | 0.296 | 0.314 |
| C(4) | 0.228 | 0.243 | 0.313 |
| C(5) | 0.203 | 0.264 | 0.295 |
| C(6) | 0.197 | 0.266 | 0.379 |
| C(1-2) | 0.240 | 0.277 | 0.750 |
| C(4-5) | 0.222 | 0.262 | 0.295 |
| C(3-6) | 0.281 | 0.298 | 0.316 |
| C(1M) | 0.203 | 0.351 | 0.843 |
| C(2M) | 0.252 | 0.332 | 0.774 |
| C(3M) | 0.232 | 0.366 | 0.396 |
| C(4M) | 0.230 | 0.314 | 0.353 |
| C(5M) | 0.248 | 0.302 | 0.353 |
| C(6M) | 0.228 | 0.298 | 0.487 |

equidistant from the methyl carbons with methyl and methylene hydrogens at maximum relative contact distances and all C-H distances set at 1.00 Å. After two isotropic cycles for the well-behaved hydrogens with all else fixed, the final R and R_w factors were at 0.084 and 0.118. For the varied hydrogens the average final shift over error in B was 0.68 and in position was 0.60. The final refinement characteristics are summarized in Table II. Programs used have been described.¹⁸

The error in an observation of unit weight, Erf, was such that the Cruickshank scheme slightly underestimated the errors. Using unit weights the R_w value is about 1% lower. These differences, however, are not expected to affect the positions of the atoms significantly at the particular level of refinement.

The intraatomic and interatomic (between adjacent atoms) correlation elements from the last nonhydrogen refinement cycle were largest (about ± 0.3) for the carbons in the acac ring associated with O(1) and O(2). No abnormal values were otherwise observed. The final electron density difference map contained most of the high residual densities in the region of the above carbons. The largest,

1.23 and -0.95 e/Å³, were in the region of C(1-2). The atomic position and thermal parameters are presented in Tables III-V.

Discussion of the Results

Cell constants for the various reported crystals of manganese(III) acetylacetonate and the cobalt(III) analog are presented in Table VI. These data, as well as a plot of the M-O distance as a function of atomic number for the tris(acetylacetonates) of the first transition series, strongly suggest that the crystal which was examined by Morosin and Brathovde¹ and which was thought to be Mn(acac)₃ was very likely Co(acac)₃. Electronic spectral data in the visible region for the solid Mn(acac)₃ had been shown to be similar² to that of solid Mn(trop)₃. The distorted MnO₆ geometries now found for these species are compatible with the assignment suggested by Davis, *et al.*,² for the observed d-d electronic transitions.

During the early stages of the refinement it became apparent that the Mn-O bonds in Mn(acac)₃ were considerably longer than those reported by MB. The final refinement indicated an average Mn-O bond to be 1.98 Å, in agreement with the value found⁶ in Mn(trop)₃ and between the bounds suggested by Forman and Orgel.²⁷ The anticipated tetragonal distortion was there, but surprisingly the MnO₆ octahedron appears to be compressed.²⁸

The most likely description of the Mn-O bond lengths (using the χ^2 test^{29,30}) in Mn(acac)₃ suggests four long bonds averaging 2.00 Å and two short bonds averaging 1.95 Å although a rhombic description also is reasonable. The various significant intramolecular distances and angles are presented

(27) A. Forman and L. E. Orgel, *Mol. Phys.*, **2**, 362 (1959).

(28) V. Day, private communication, has informed us of the existence of another monoclinic Mn(acac)₃ crystalline modification designated to be γ -Mn(acac)₃. The MnO₆ octahedron is elongated in this crystal.

(29) P. R. Bevington, "Data Reduction and Error Analysis for Physical Sciences," McGraw-Hill, New York, N. Y., 1969, Chapters 2, 5, and 10.

(30) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, Section 18.6.

Table VI. Cell Dimensions Found for Manganese(III) and Cobalt(III) Acetylacetonates

| | Manganese(III) | | | | | | | Cobalt(III) | |
|---------------|----------------|--------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|--|-----------------------------|----------------|
| | Astbury (1926) | Morosin-Brathovde (1964) | Pfluger ^a (1965) | Morosin ^a (1972) | α -Mn Fackler-Avdeef | β -Mn Fackler-Avdeef | γ -Mn, V. W. Day, <i>et al.</i> | Morosin ^a (1972) | Pfluger (1973) |
| <i>a</i> , Å | 14.1 | 13.875 | 14.046 | 14.052 | ~15.4 | 14.013 | 7.786 | 13.923 | 13.951 |
| <i>b</i> , Å | 7.68 | 7.467 | 7.617 | 7.618 | ~13.6 | 7.599 | 27.975 | 7.473 | 7.470 |
| <i>c</i> , Å | 16.5 | 16.203 | 16.442 | 16.442 | ~16.6 | 16.373 | 8.020 | 16.248 | 16.222 |
| β , deg | 99.4 | 98.427 | 99.43 | 99.36 | | 99.33 | 100.34 | 98.50 | 98.48 |

^a Private communication.Table VII. Significant Intramolecular Distances and Estimated Standard Deviations in Mn(acac)₃ (Å)

| | | | |
|---------------|---------------------------|-------------------------|---------------|
| Mn-O(1) | 1.931 (10) ^a | C(1)-C(1M) | 1.574 (26) |
| Mn-O(3) | 1.956 (7) | C(2)-C(2M) | 1.524 (26) |
| Mean | 1.948 (17) ^c | C(3)-C(3M) | 1.543 (16) |
| | [4.19, 4.1%] ^d | C(4)-C(4M) | 1.522 (16) |
| Mn-O(2) | 1.991 (7) | C(5)-C(5M) | 1.538 (15) |
| Mn-O(4) | 1.984 (8) | C(6)-C(6M) | 1.543 (17) |
| Mn-O(5) | 2.020 (7) | Weighted mean | 1.538 (15) |
| Mn-O(6) | 2.003 (8) | | [0.68, 64.0%] |
| Mean | 2.000 (17) | O(1)··O(2) ^b | 2.777 (10) |
| | [4.65, 0.30%] | O(3)··O(6) | 2.786 (11) |
| O(1)-C(1) | 1.235 (21) | O(4)··O(5) | 2.813 (11) |
| O(2)-C(2) | 1.244 (15) | Mean | 2.791 (18) |
| O(3)-C(3) | 1.254 (13) | | [3.08, 4.6%] |
| O(4)-C(4) | 1.269 (12) | O(1)··O(4) | 2.754 (14) |
| O(5)-C(5) | 1.261 (13) | O(1)··O(5) | 2.790 (12) |
| O(6)-C(6) | 1.263 (16) | O(1)··O(6) | 2.817 (12) |
| Weighted mean | 1.257 (12) | O(2)··O(3) | 2.831 (10) |
| | [0.63, 67.9%] | O(2)··O(5) | 2.832 (10) |
| C(1)-C(1-2) | 1.346 (28) | O(2)··O(6) | 2.813 (11) |
| C(2)-C(1-2) | 1.423 (23) | O(3)··O(4) | 2.756 (9) |
| C(3)-C(3-6) | 1.400 (17) | O(3)··O(5) | 2.795 (9) |
| C(4)-C(4-5) | 1.395 (16) | O(4)··O(6) | 2.813 (11) |
| C(5)-C(4-5) | 1.364 (15) | Mean | 2.801 (30) |
| C(6)-C(3-6) | 1.397 (19) | | [7.54, 0.00%] |
| Weighted mean | 1.388 (24) | C(4-5)-H45 | 0.95 (14) |
| | [1.61, 15.4%] | C(4M)-H4M1 | 0.83 (13) |
| | | C(4M)-H4M2 | 1.26 (16) |
| | | C(4M)-H4M3 | 0.84 (13) |
| | | C(5M)-H5M1 | 0.97 (15) |
| | | C(5M)-H5M2 | 1.10 (16) |
| | | C(5M)-H5M3 | 1.01 (16) |
| | | Mean | [1.39, 21.5%] |

^a The individual esd values, σ_i , are based on the diagonal values of the least-squares symmetric matrix. ^b The "bite" distance. ^c Weighted mean, \bar{l} , and esd, s , are based on the dispersion about the mean, and are defined as $\bar{l} = \sum w_i l_i / \sum w_i$; $s = \{ [N \sum w_i (l_i - \bar{l})^2] / (N-1) \cdot \sum w_i \}^{1/2}$; $w_i = \sigma_i^{-2}$. ^d The first value in the brackets refers to the reduced $\chi_r^2 = (s^2/N) \sum w_i$. The second value refers to the probability that a random distribution of equal bonds would give a value of χ_r^2 as large as that calculated. See ref 29.

in Tables VII and VIII. The various dimensions, the labeling scheme, and the weighted mean acetylacetonate dimensions are presented in Figure 1. The thermal ellipsoid drawing is also shown in the figure, as are two short bonds, averaging 1.948 Å. The various significant intramolecular distances and angles are presented in Tables VII and VIII. The various dimensions, the labeling scheme, and the weighted mean acetylacetonate dimensions are presented in Figure 1. The thermal ellipsoid drawing is also shown in the figure.

Molecular Packing of Tris(acetylacetonates). Most neutral M(acac)₃ complexes of the first- and second-row transition series are related isomorphically in either a monoclinic or an orthorhombic cell (Table VI). Both types of packing are observed in the case of Mn(acac)₃. The unit cell is shown in Figure 2.

The monoclinic class ($P2_1/c$), M = Al, Cr, β -Mn, Co, and Rh, has $a = 13.94$ - 14.07 Å, $b = 7.47$ - 7.60 Å, $c = 16.22$ - 16.53 Å, and $\beta = 98.5$ - 99.4° . (Both β -V and γ -Mn crystal-

lize in a different monoclinic cell.) All of the molecules in this class pack identically. In each case the acac ligand containing oxygens 1 and 2 shows high anisotropic thermal parameters. The packing of this acac ring does not appear to be loose²² since some of the shortest contacts occur between these rings (Figures 3 and 4). Morosin,²¹ observing the effect in Cr(acac)₃, pursued it further by examining the low-temperature (-65°) film data and concluded that the ellipsoids were of thermal origin rather than based on disorder since certain room-temperature diffuse reflections sharpened considerably upon cooling. He suggested that the rings participate in longitudinal lattice vibrations.

The orthorhombic class (*Pbca*) is observed for M = Sc, α -V, α -Mn, and Fe, with $a = 15.38$ - 15.53 Å, $b = 13.34$ - 13.73 Å, and $c = 16.57$ - 16.73 Å.

Trigonal Distortions. The average twist angle and compression ratio, $\phi = 60.2^\circ$ and $s/h = 1.241$,⁶ indicate very little trigonal distortion from the regular octahedral shape for Mn(acac)₃. Figure 5 shows the MnO₆ octahedron along with the various bite distances. The lack of distortion is consistent with the larger bite distance in Mn(acac)₃ than in Mn(trop)₃ based on the previous simple argument.⁶

The Acetylacetonate Ligand. The number of reported structures containing the acac ligand is very large. For example, ref 31 notes 127 structures reported before 1971. A few years ago Lingafelter³² compared the dimensions of the various known acac-containing structures. He noted that the distances (see Figure 1c for labeling scheme) O-C, C-C_b, C-C_m and angles O-C-C_b, C-C_b-C, O-C-C_m were within experimental error invariant.

Table IX shows the structural dimensions of some monomeric (acac)₃ complexes. The dimensions reported for the ligands in Mn(acac)₃ compare well with those in the other structures. The acac ligands in Mn(acac)₃ are nearly planar, as is shown in Table X.

Crystal Field Calculation of the Jahn-Teller Distortion.

Table XI summarizes the available crystallographic structural data for compounds susceptible to strong JT forces. Although the majority of the compounds are polymeric ionic solids, requiring caution in attempts to characterize³³ the distortions, there are enough examples of discrete molecular complexes to indicate that the JT distortions take on a variety of forms in the solid state.

We decided to reexamine the Liehr and Ballhausen³⁴ model for the Jahn-Teller distortion and apply it to Mn(acac)₃ for the following reasons: (a) the correct solid-state structure of the compound is known; (b) at least one crystalline modi-

(31) O. Kennard and D. G. Watson, Ed., "Molecular Structures and Dimensions," Crystallographic Data Centre, Cambridge, and the Union of Crystallography, Utrecht, Vol. II, 1970, p 140 ff; Vol. III, 1971, p 292 ff.

(32) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

(33) M. D. Sturge, *Solid State Phys.*, **20**, 91 (1967).

(34) A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (New York)*, **3**, 304 (1958).

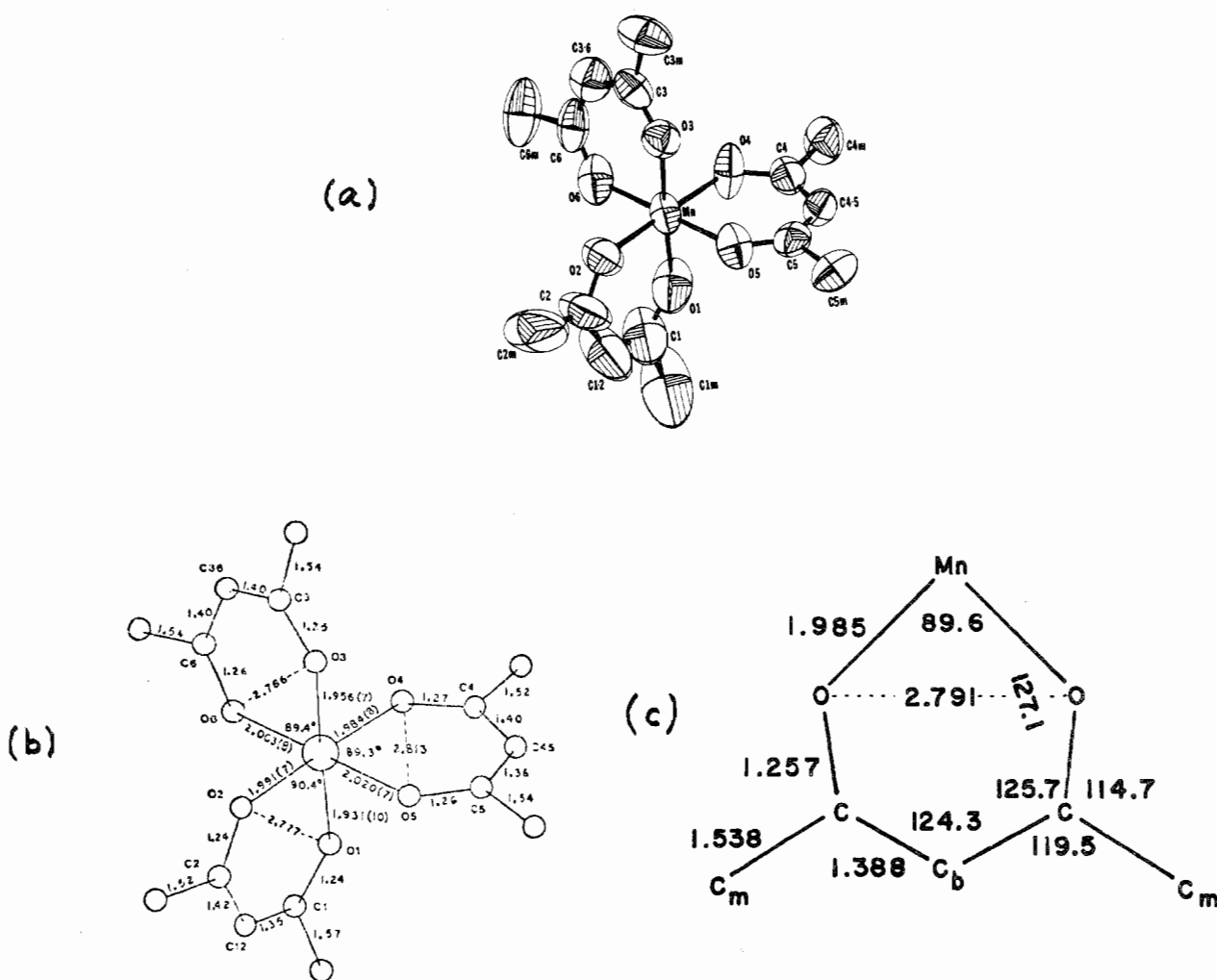


Figure 1. $\text{Mn}(\text{acac})_3$: (a) ORTEP thermal ellipsoid view (50% probability level) and the numbering scheme; (b) the dimensions; (c) the weighted mean dimensions. See Tables VI and VII.

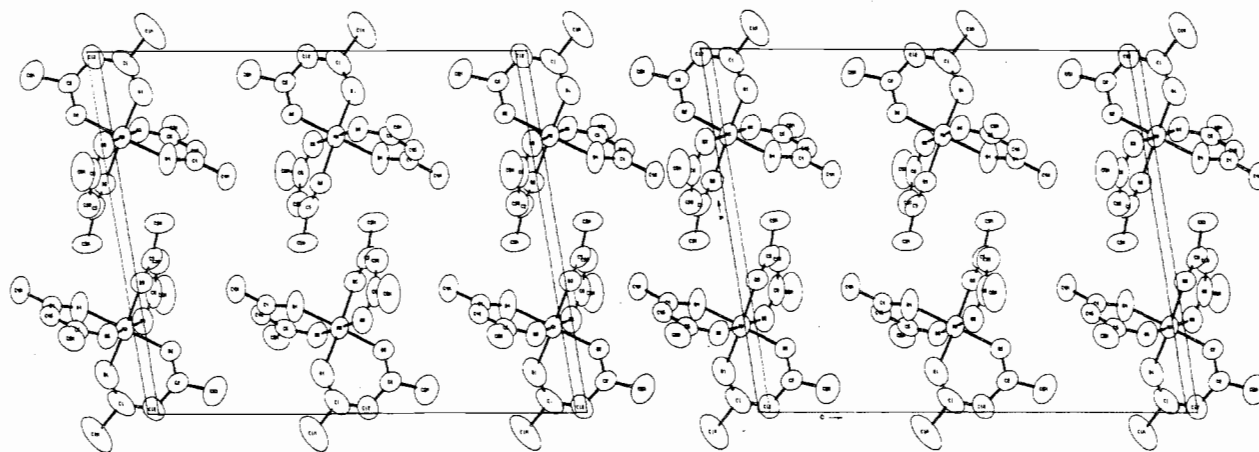


Figure 2. An ORTEP stereopair drawing of the $\text{Mn}(\text{acac})_3$ cell projected perpendicular to the b axis (50% probability ellipsoids).

fication indicates a tetragonally compressed MnO_6 octahedron (which the model predicts); (c) better radial functions are now available; (d) the force constants for the molecule can be estimated reasonably well from available vibrational spectroscopic data.

Liehr and Ballhausen expanded the potential energy of the E_g state in terms of the displacement coordinates, shown in Figure 6, in a Taylor series. The secular determinant in the basis of distorted functions was solved and the two

levels resulting from the lifting of the degeneracy of the original E_g state have the energies

$$E_{\pm}(q_1, q_2, \phi_2) = (1/2)k_1q_1^2 + (1/2)k_2q_2^2 + (1/\sqrt{6})B_1q_1 \pm (1/2)q_2[\alpha^2 + \beta^2q_2^2 + 4\beta^2(2q_1^2 - \sqrt{2}q_1q_2 \cos 3\phi_2) - 2\alpha\beta(q_2 \cos 3\phi_2 - 2\sqrt{2}q_1)]^{1/2}$$

where $\alpha = 4\sqrt{3}[(1/7)B_2 + (5/84)B_4]$ and $\beta = (1/7)C_2 +$

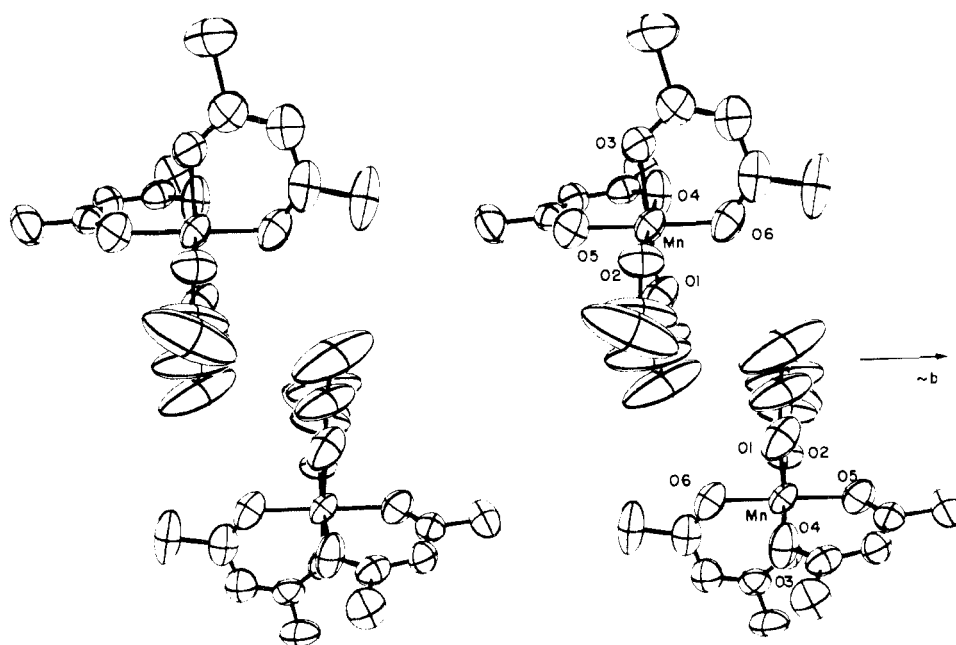


Figure 3. An ORTEP/II stereopair drawing of the packing region in $\text{Mn}(\text{acac})_3$, viewed perpendicular to the acac ring containing O(1) and O(2) (50% probability level ellipsoids). The two molecules are related as (x, y, z) and $(-x, 1-y, 1-z)$, contrary to what is said in ref 21.

Table VIII. Significant Intramolecular Angles and Estimated Standard Deviations in $\text{Mn}(\text{acac})_3$, (deg)^a

| | | | |
|---------------------------|---------------|-------------------|---------------|
| O(1)-Mn-O(2) ^b | 90.2 (4) | C(1)-C(1-2)-C(2) | 125.7 (16) |
| O(4)-Mn-O(5) | 89.3 (4) | C(3)-C(3-6)-C(6) | 123.3 (9) |
| O(3)-Mn-O(6) | 89.4 (4) | C(4)-C(4-5)-C(5) | 124.7 (7) |
| Mean | 89.6 (5) | Mean | 124.3 (10) |
| | [1.52, 21.9%] | | [1.16, 31.3%] |
| O(1)-Mn-O(4) | 89.4 (4) | O(1)-C(1)-C(1M) | 113.4 (14) |
| O(1)-Mn-O(5) | 89.8 (4) | O(2)-C(2)-C(2M) | 114.2 (13) |
| O(1)-Mn-O(6) | 91.4 (4) | O(3)-C(3)-C(3M) | 116.0 (80) |
| O(2)-Mn-O(3) | 91.7 (3) | O(4)-C(4)-C(4M) | 114.3 (7) |
| O(2)-Mn-O(5) | 89.9 (3) | O(5)-C(5)-C(5M) | 114.8 (7) |
| O(2)-Mn-O(6) | 89.6 (4) | O(6)-C(6)-C(6M) | 114.5 (9) |
| O(3)-Mn-O(4) | 88.8 (3) | Mean | 114.7 (8) |
| O(3)-Mn-O(5) | 89.3 (3) | | [0.81, 54.3%] |
| O(4)-Mn-O(6) | 91.3 (4) | C(1M)-C(1)-C(1-2) | 119.8 (16) |
| Mean | 90.1 (11) | C(2M)-C(2)-C(1-2) | 123.3 (15) |
| | [9.94, 0.00%] | C(3M)-C(3)-C(3-6) | 117.7 (9) |
| O(1)-Mn-O(3) | 178.0 (4) | C(4M)-C(4)-C(4-5) | 120.1 (8) |
| O(2)-Mn-O(4) | 179.0 (4) | C(5M)-C(5)-C(4-5) | 118.8 (8) |
| O(5)-Mn-O(6) | 178.6 (4) | C(6M)-C(6)-C(3-6) | 120.3 (10) |
| Mean | 178.5 (6) | Mean | 119.5 (16) |
| | [1.58, 20.5%] | | [2.48, 3.0%] |
| Mn-O(1)-C(1) | 127.6 (10) | H4M1-C(4M)-H4M2 | 94.3 (68) |
| Mn-O(2)-C(2) | 127.5 (9) | H4M1-C(4M)-H4M3 | 127.0 (65) |
| Mn-O(3)-C(3) | 127.3 (6) | H4M2-C(4M)-H4M3 | 120.7 (71) |
| Mn-O(4)-C(4) | 127.2 (6) | H5M1-C(5M)-H5M2 | 120.7 (71) |
| Mn-O(5)-C(5) | 126.4 (6) | H5M1-C(5M)-H5M3 | 102.7 (62) |
| Mn-O(6)-C(6) | 127.0 (7) | H5M2-C(5M)-H5M3 | 103.3 (62) |
| Mean | 127.1 (5) | Mean | 110.8 (129) |
| | [0.39, 85.5%] | | [3.79, 0.25%] |
| O(1)-C(1)-C(1-2) | 126.4 (14) | | |
| O(2)-C(2)-C(1-2) | 122.3 (13) | | |
| O(3)-C(3)-C(3-6) | 126.3 (8) | | |
| O(4)-C(4)-C(4-5) | 125.6 (7) | | |
| O(5)-C(5)-C(4-5) | 126.4 (7) | | |
| O(6)-C(6)-C(3-6) | 125.1 (9) | | |
| Mean | 125.7 (12) | | |
| | [1.82, 10.5%] | | |

^a See the footnotes in Table VII. ^b The "bite" angles.

(5/84) C_4 . The force constants k_1 and k_2 refer to a_{1g} and e_g vibrations, respectively. The B_k and C_k integrals are defined to be negative compared to those described by Ballhausen and Ancom.³⁵ The published values of the integrals can be used only with Slater radial functions. In

order to utilize SCF atomic radial functions, these integrals were derived in a more general form, and the details are presented in the Appendix.

(35) C. J. Ballhausen and E. M. Ancom, *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, 31 (9), 1 (1958).

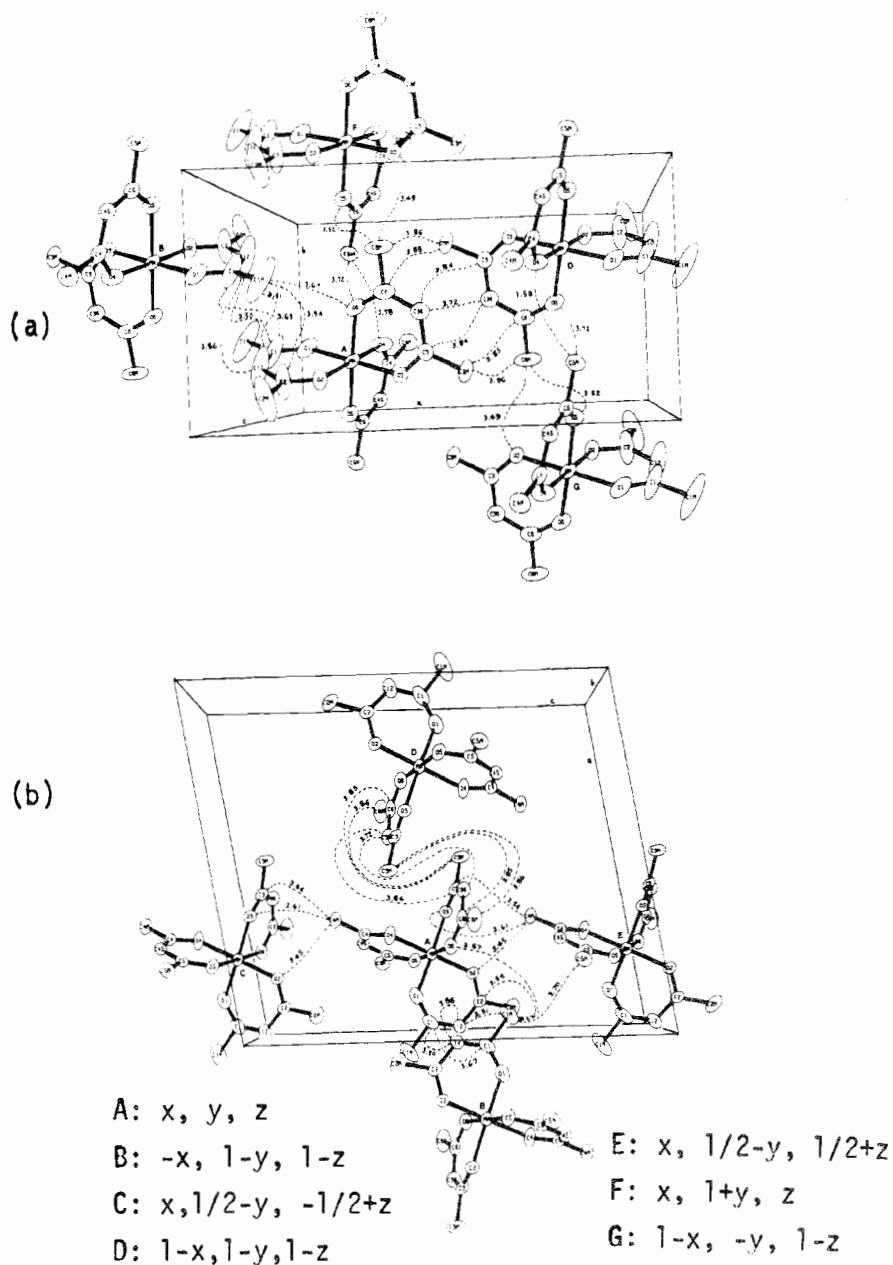


Figure 4. Two perspective views of cell packing in $\text{Mn}(\text{acac})_3$ (ellipsoids drawn at 20% probability level), along with intermolecular contact distances ($<3.87 \text{ \AA}$): (a) viewed above the ab plane; (b) viewed above the ac plane.

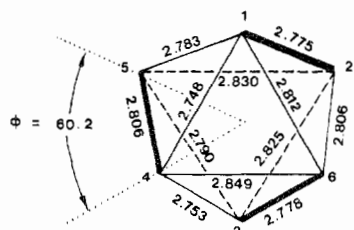


Figure 5. The MnO_6 polyhedron in $\text{Mn}(\text{acac})_3$. The thick edges refer to the bite distances and ϕ is the average twist angle.

Using the force constants $k_1 = k_2 = 1.69 \text{ mdyn/\AA}^{36}$ and Richardson's³⁷ neutral double- ζ ($3d^5s^2$ configuration) 3d radial function

$$R(r) = 0.514x(3d, 5.51) + 0.693x(3d, 1.70)$$

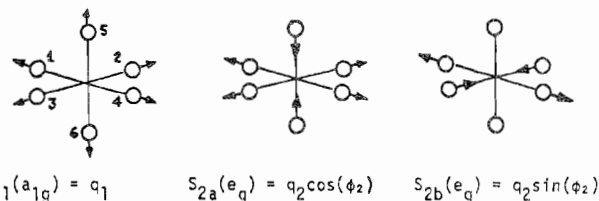


Figure 6. Displacements along the octahedral a_{1g} and e_g symmetry coordinates. Circles represent undistorted nuclear positions.

where $x(nl, \zeta) = [(2\zeta)^{n+1}/(2n)!]^{1/2} r^{n-1} \exp(-\zeta r)$, the calculated results are summarized in Table XI.

The barrier to pseudorotation is thus calculated to be 60 cm^{-1} , which is only slightly higher than the value of kT at liquid nitrogen temperature. Since the barrier is negligible at room temperature, the wave functions describing the two

(36) J. P. Fackler, Jr., and A. Avdeef, to be submitted for publication.

(37) J. W. Richardson, W. C. Nieuwoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1957 (1962).

Table IX. Structures of Tris(acetylacetonato) Complexes^a

| Species | Space group Vol/ mole- cule, Å ³ | a, Å b, Å (β, deg) c, Å | Distances, Å | | | | | Angles, deg | | | | | | Ref |
|--------------------------------------|--|----------------------------------|--------------|-------|-------|------------------|------------------|-------------|-------|--------------------|---------------------|--------------------|----------------------------------|-----------|
| | | | M-O | O···O | O-C | C-C _b | C-C _m | O-M-O | M-O-C | O-C-C _b | C-C _b -C | O-C-C _m | C _b -C-C _m | |
| Al(acac) ₃ | P2 ₁ /c 431 | 14.069 7.568 (99.0) 16.377 | 1.892 | 2.726 | 1.283 | 1.380 | 1.547 | 91.8 | 127.7 | 125.3 | 122.6 | 114.1 | 120.6 | 22 |
| Sc(acac) ₃ | Pbca 441 | 15.38 13.73 16.72 | 2.070 | 2.715 | 1.253 | 1.381 | 1.506 | 82.0 | 132.5 | 124.4 | 119.4 | 116.1 | 119.5 | 15 |
| α-V(acac) ₃ | Pbca 433 | 15.43 13.53 16.60 | 1.979 | 2.749 | 1.256 | 1.383 | 1.518 | 88.0 | 128.8 | 124.9 | 124.0 | 114.3 | 120.7 | 16 |
| β-V(acac) ₃ | P2 ₁ /c 433 | 16.34 13.06 (90.2) 8.108 | 1.982 | 2.736 | 1.262 | 1.391 | 1.518 | 87.3 | 131.7 | 123.9 | 124.7 | 116.2 | 120.2 | 16 |
| Cr(acac) ₃ | P2 ₁ /c 428 | 14.031 7.551 (99.1) 16.379 | 1.951 | 2.786 | 1.263 | 1.388 | 1.517 | 91.1 | 127 | 125 | 125 | 115 | 120 | 21 |
| α-Mn(acac) ₃ | Pbca 433 | 15.530 13.339 16.726 | | | | | | | | | | | | This work |
| β-Mn(acac) ₃ | P2 ₁ /c 430 | 14.013 7.600 (99.3) 16.373 | 1.985 | 2.791 | 1.257 | 1.388 | 1.538 | 89.6 | 127.1 | 125.7 | 124.3 | 114.7 | 119.5 | This work |
| Fe(acac) ₃ | Pbca 435 | 15.471 13.577 16.565 | 1.992 | 2.744 | 1.258 | 1.377 | 1.530 | 87.1 | 129.3 | 125.0 | 124.8 | 114.9 | 120.6 | 14 |
| Co(acac) ₃ | P2 ₁ /c 418 | 13.951 7.470 (98.5) 16.222 | 1.898 | 2.850 | 1.269 | 1.382 | 1.544 | 97.3 | 121.8 | 127.5 | 123.6 | 112.9 | 119.6 | 22 |
| (Mn(acac) ₃ (MB)) | P2 ₁ /c 415 | 13.875 7.467 (98.4) 16.203 | 1.872 | 2.805 | 1.288 | 1.378 | 1.515 | 97.0 | 123.2 | 125.6 | 124.9 | 113.7 | 120.6 | 1 |
| Rh(acac) ₃ | P2 ₁ /c 428 | 13.925 7.483 (98.6) 16.392 | 1.992 | 2.944 | 1.272 | 1.383 | 1.503 | 95.3 | 121.8 | 126.4 | 128.0 | 113.0 | 120.8 | b |
| Eu(DPM) ₃ | | | 2.21 | 2.67 | 1.27 | 1.40 | 1.56 | 74.4 | 137.7 | 123.8 | 122.6 | 114.1 | 122.3 | c |
| Mg(hfacac) ₃ ⁻ | | | 2.058 | 2.770 | 1.26 | 1.38 | 1.49 | 84.6 | 127 | 127 | 123 | 116 | 117 | d |
| Co(acac) ₃ ⁻ | | | 1.981 | | | | | 91.5 | | | | | | e |
| Ni(acac) ₃ ⁻ | | | 2.04 | 2.88 | 1.30 | 1.38 | 1.54 | 90 | 120 | 127 | 123 | 113 | 122 | f |
| Cu(hfacac) ₃ ⁻ | | | 2.067 | 2.862 | 1.26 | 1.39 | 1.50 | 87.6 | 124 | 129 | 122 | 114 | 117 | d |
| Av dimensions | | | | 2.764 | 1.279 | 1.384 | 1.527 | | | 125.7 | 123.3 | 114.6 | 119.9 | |

^a The atomic labeling scheme is presented in Figure 1c. ^b J. C. Morrow and E. B. Parker, Jr., *Acta Crystallogr., Sect. B*, 29, 1145 (1973).

^c J. P. F. de Villiers and J. C. A. Boeyens, *ibid.*, 28, 2335 (1972). ^d M. R. Truter and B. V. Vickery, *J. Chem. Soc., Dalton Trans.*, 395 (1972). ^e B. Granoff, *Diss. Abstr. B*, 27, 4341 (1967). ^f W. H. Watson and C.-T. Lin, *Inorg. Chem.*, 5, 1074 (1966).

JT levels of the molecule in solution are time dependent (according to the model)

$$\begin{pmatrix} \psi_{\text{upper level}} \\ \psi_{\text{lower level}} \end{pmatrix} = \begin{pmatrix} \cos \phi_2/2 & \sin \phi_2/2 \\ \sin \phi_2/2 & -\cos \phi_2/2 \end{pmatrix} \begin{pmatrix} \psi_{d_{x^2-y^2}} \\ \psi_{d_{z^2}} \end{pmatrix}$$

where $\phi_2 = \omega_{\text{exchange}t}$.

It is of interest to relate the q_1 and q_2 coordinates to actual internal displacement coordinates. In matrix form the displacements depicted in Figure 6 can be stated as $S = q = A\Delta r$, where the column matrices S , Δr , and q have elements (S_1, S_{2a}, S_{2b}) , $(\Delta r_1, \dots, \Delta r_6)$, and $(q_1, q_2 \cos \phi_2, q_2 \sin \phi_2)$, respectively, and

$$A = \begin{bmatrix} \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \\ \frac{1}{2\sqrt{3}} & \frac{1}{2\sqrt{3}} & \frac{1}{2\sqrt{3}} & \frac{1}{2\sqrt{3}} & \frac{-1}{\sqrt{3}} & \frac{-1}{\sqrt{3}} \\ \frac{1}{2} & \frac{-1}{2} & \frac{1}{2} & \frac{-1}{2} & 0 & 0 \end{bmatrix}$$

Since $A^\dagger A$ is a singular matrix, Δr can only be solved in-

directly. However, the expression $A^\dagger A \Delta r = A^\dagger q$ reduces the problem.

When it is taken into account that S_1 , S_{2a} , and S_{2b} possess inversion symmetry, one obtains the solutions (positive Δr is in the direction away from the metal) (cf. footnote 10, ref 34).

$$\Delta r_1 = \Delta r_3 = \frac{1}{\sqrt{6}}q_1 + \frac{1}{2\sqrt{3}}q_2 \cos \phi_2 + \frac{1}{2}q_2 \sin \phi_2$$

$$\Delta r_2 = \Delta r_4 = \Delta r_1 - q_2 \sin \phi_2$$

$$\Delta r_5 = \Delta r_6 = \frac{1}{\sqrt{6}}q_1 - \frac{1}{\sqrt{3}}q_2 \cos \phi_2$$

For an arbitrary value of ϕ_2 , the octahedron is distorted orthorhombically. The distortions in $\text{Mn}(\text{acac})_3$ are calculated from q_1 and q_2 to be (cf. Table XII)

$$\begin{array}{l} \text{case 1} \} \\ \text{case 2} \} \Delta r_{\text{equatorial}} = +0.013 \text{ \AA}, \Delta r_{\text{axial}} = -0.092 \text{ \AA} \\ \text{case 3} \} \\ \text{case 4} \} \Delta r_{\text{equatorial}} = -0.053 \text{ \AA}, \Delta r_{\text{axial}} = +0.041 \text{ \AA} \end{array}$$

These correspond to shifts from the value 1.985 Å.

Assuming the same force constants used for $\text{Mn}(\text{acac})_3$,

Table X. Least-Squares-Fitted Planes in $\text{Mn}(\text{acac})_3$

| | | I. Deviations from the Mean Planes (in Å) | | | | | |
|---------------|--------|---|-----------|------------|-----------|-----------|-----------|
| | | Plane A | Plane B | Plane C | Plane D | Plane E | Plane F |
| acac A | Mn | | | | -0.012 | -0.008 | 0.006 |
| | O(1) | -0.004 | | | 0.002 | 0.023 | |
| | C(1) | -0.046 | | | | | |
| | C(1M) | 0.024 | | | | | |
| | C(1-2) | 0.005 | | | | | |
| | C(2M) | -0.021 | | | | | |
| acac B | O(2) | 0.032 | | | | | |
| | O(4) | -0.009 | | | 0.004 | | 0.013 |
| | C(4) | | -0.025 | | 0.003 | | 0.013 |
| | C(4M) | | 0.008 | | | | |
| | C(4-5) | | 0.001 | | | | |
| | C(5M) | | 0.013 | | | | |
| acac C | C(5) | | -0.023 | | | | |
| | O(5) | | 0.010 | | | | |
| | O(3) | | 0.017 | | | 0.007 | -0.016 |
| | C(3) | | | -0.038 | 0.002 | 0.023 | |
| | C(3M) | | | 0.020 | | | |
| | C(3-6) | | | -0.024 | | | |
| Rms dev (esd) | C(6M) | | | 0.061 | | | |
| | C(6) | | | -0.052 | | | |
| | O(6) | | | 0.013 | | | |
| | | | | 0.020 | | 0.007 | -0.016 |
| | | 0.025 (25) | 0.016 (9) | 0.037 (11) | 0.006 (7) | 0.019 (7) | 0.014 (6) |

II. Equations of the Mean Planes

$$\begin{aligned} \text{A: } & 0.0125x + 0.9181y + 0.3960z = 4.9660 & \text{D: } & 0.0763x + 0.9182y + 0.3886z = 4.9514 \\ \text{B: } & 0.8589x - 0.2872y + 0.4240z = 4.5116 & \text{E: } & 0.5481x + 0.2966y - 0.7821z = -4.2466 \\ \text{C: } & 0.4220x + 0.2561y - 0.8697z = -5.4591 & \text{F: } & 0.8278x - 0.2814y + 0.4854z = 4.8404 \end{aligned}$$

III. Dihedral Angles between Some of the Planes

| | A | B | C | D | E | F |
|---|------|------|-----|------|------|---|
| A | 0 | | | | | |
| B | 94.8 | 0 | | | | |
| C | 84.0 | 85.4 | 0 | | | |
| D | 3.7 | | | 0 | | |
| E | | | 9.1 | 90.6 | 0 | |
| F | | 4.0 | | 90.4 | 89.5 | 0 |

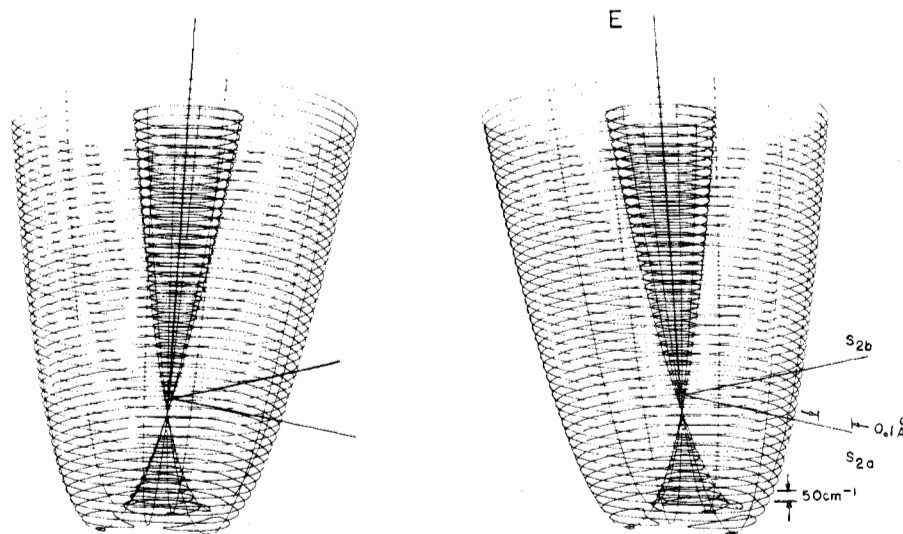


Figure 7. Stereopair view of the potential energy surface in the Jahn-Teller distorted $\text{Mn}(\text{acac})_3$, according to the crystal field model. The S_{2a} ($=q_2 \cos \phi_2$) and S_{2b} ($=q_2 \sin \phi_2$) axes are drawn 0.5 Å long, and the energy axis is drawn 0–2000 cm^{-1} . The a_{1g} distortion coordinate, q_1 , is -0.052 Å. The trough positions in the tetragonally compressed structure correspond to -672 cm^{-1} , $\phi_2 = 0, \pm 2\pi/3$, and the barrier to exchange (saddle points, $\phi_2 = \pi, \pm \pi/3$) is 60 cm^{-1} .

the distortions calculated for $\text{Mn}(\text{trop})_3$ are slightly smaller.⁶

Figure 7 shows the calculated potential energy surface for $\text{Mn}(\text{acac})_3$, computer-drawn as a stereopair projection.

Conclusions

The structure of $\text{Mn}(\text{acac})_3$ reported here eliminates the principal crystallographic anomaly occurring in the literature for a complex supposedly susceptible to Jahn-Teller forces,

but showing no structural distortion. Other systems with "equivalent" metal-ligand bond lengths show temperature-dependent properties implying the presence of a fluxional molecule describable by a dynamic JT formalism,³⁸ or the metal ion is found at a position of high crystallographic sym-

(38) (a) J. Pradilla-Sorzano and J. P. Fackler, Jr., *Inorg. Chem.*, **12**, 1182 (1973); (b) B. V. Harrowfield and J. R. Pilbrow, *Proc. Phys. Soc., London (Solid State Phys.)*, **6**, 755 (1973).

Table XI. Structures of Octahedral Homoligand Complexes Containing d^4 (High Spin), d^7 (Low Spin), or d^9 Electronic Configurations

| Compd ^a | Chromophore | Space group | Bonds, ^b Å | | | Comments | Ref |
|---|-------------------|---|---|------------|---|---|------|
| | | | Group A. Elongated Tetragonal Distortion | | | | |
| | | | Axial | Equat | | | |
| (K ₂ Na)[MnF ₆] | MnF ₆ | <i>F4/mmm</i> | 2.06 | 1.86 | Discrete MnF ₆ ³⁻ species | 7 | |
| CS ₂ KMnF ₆ | MnF ₆ | <i>F4/mmm</i> | 2.07 | 1.92 | Pesovskite-like | c | |
| (NH ₄) ₂ MnF ₅ | MnF ₆ | <i>Pnma</i> | 2.10 | 1.85 | Fluoride-bridged infinite chains | d | |
| K ₂ MnF ₅ ·H ₂ O | MnF ₆ | <i>P2₁/n</i> | 2.07 | 1.83 | Chain polymer with shared corners | e | |
| Mn(trop) ₃ , 1 | MnO ₆ | <i>P2₁/c</i> | 2.13 | 1.94 | | 5, 6 | |
| Mn(Et ₂ dtc) ₃ | MnS ₆ | <i>P2₁/a</i> | 2.55 | 2.38, 2.43 | | g | |
| CrF ₂ | CrF ₆ | <i>P2₁/n</i> | 2.43 | 1.99 | Rutile-like, shared corners | f | |
| CrCl ₂ | CrCl ₆ | <i>Pnnm</i> | 2.92 | 2.40 | Infinite planar structure | g | |
| CrI ₂ | CrI ₆ | <i>C2/m</i> | 3.24 | 2.74 | Infinite planar structure | h | |
| CuF ₂ | CuF ₆ | <i>P2₁/n</i> | 2.27 | 1.93 | Rutile-like | i | |
| CuCl ₂ | CuCl ₆ | | 2.95 | 2.30 | Chains linked into layers | j | |
| CuBr ₂ | CuBr ₆ | <i>A2</i> | 3.18 | 2.40 | Similar to CuCl ₂ | k | |
| CsCuCl ₃ | CuCl ₆ | <i>P6₃/22</i> | 2.78 | 2.28, 2.36 | Face-shared polymer | l | |
| Na ₂ CuF ₄ | CuF ₆ | <i>P2₁/c</i> | 2.37 | 1.91 | Polymer | m | |
| K ₂ CuF ₆ | CuF ₆ | <i>I4/mmm</i> | | 4F < 2F | c axis larger than in ref v | m | |
| Tl ₂ [Cu(SO ₃) ₂] | CuO ₆ | <i>P1</i> | 2.44 | 1.99 | | n | |
| [Cu(1,2-ethanediol) ₃](SO ₄) | CuO ₆ | <i>P2₁/c</i> | 2.33 | 2.00 | δδδ confign | o | |
| (bdanH)[Cu(hfacac) ₃] | CuO ₆ | <i>P2₁/n</i> | 2.18 | 2.01 | | p | |
| [Cu(H ₂ O) ₆][SiF ₆] | CuO ₆ | <i>R3</i> | 2.37 | 1.97 | $\bar{1}$ site symmetry; cf. group D | q | |
| (-) ₃₈₉ -[Cu(<i>l</i> -pn) ₃]Br ₂ ·2H ₂ O | CuN ₆ | <i>P2₁</i> | 2.31 | 2.09 | | r | |
| [Cu(dien) ₂]Br ₂ ·H ₂ O | CuN ₆ | <i>P2₁/c</i> | 2.43 | 2.04 | Tridentate ligand | s | |
| | | | Group B. Compressed Tetragonal Distortion | | | | |
| | | | Axial | Equat | | | |
| Mn(acac) ₃ | MnO ₆ | <i>P2₁/c</i> | 1.95 | 2.00 | | This work | |
| KCrF ₃ | CrF ₆ | | 2.00 | 2.14 | Perovskite-like | t | |
| KCuF ₃ | CuF ₆ | | 1.96 | 2.07 | Perovskite-like | t | |
| Ba ₂ CuF ₆ | CuF ₆ | <i>I2/m</i> | 1.85 | 2.08 | Infinite layer structure | u | |
| K ₂ CuF ₄ | CuF ₆ | <i>I4/mmm</i> | 1.95 | 2.08 | Cf. ref m | v | |
| [Cu(PCP) ₃](ClO ₄) ₂ | CuO ₆ | <i>Pna2₁</i> | 2.04 | 2.11 | | w | |
| [Cu(dien) ₂](NO ₃) ₂ | CuN ₆ | <i>P2₁2₁2₁</i> | 2.01 | 2.22 | Tridentate ligand | x | |
| | | | Group C. Orthorhombic Distortion | | | | |
| | | | Short | Med | Long | | |
| MnF ₃ | MnF ₆ | <i>C2/c</i> | 1.79 | 1.91 | 2.09 | Polymer | y |
| Mn(trop) ₃ , 2 | MnO ₆ | <i>P2₁/c</i> | 1.94 | 1.99 | 2.05 | | 5, 6 |
| KCuF ₆ | CuF ₆ | <i>I4/mcm</i> | 1.89 | 1.96 | 2.25 | Perovskite-like | z |
| Cu ₂ P ₄ O ₁₂ | CuO ₆ | <i>C2/c</i> | 1.92 | 1.98 | 2.42 | Polymer | aa |
| [Cu(H ₂ O) ₆](ClO ₄) ₂ | CuO ₆ | <i>P2₁/c</i> | 2.09 | 2.16 | 2.28 | Hydrogen bonding | bb |
| (NH ₄) ₂ [Cu(H ₂ O) ₆](SO ₄) | CuO ₆ | <i>P2₁/a</i> | 1.97 | 2.10 | 2.20 | "Tutton salt" | cc |
| | | | Group D. Isometric (Distortionless) | | | | |
| (K ₂ Ba)[Co(NO ₂) ₆] | CoN ₆ | <i>Fm3</i> | 1.98 | | | Low spin | dd |
| K ₃ NiF ₆ | NiF ₆ | <i>F3m3</i> | Equiv | | | Low spin | m |
| [Cu(H ₂ O) ₆][SiF ₆] | CuO ₆ | <i>R3</i> | 2.07 | | | $\bar{3}$ site symmetry; cf. group A | q |
| (K ₂ Pb)[Cu(NO ₂) ₆] | CuN ₆ | <i>Fm3</i> | 2.11 | | | <i>T_h</i> site symmetry; ellipsoids along Cu-N | ee |
| [Cu(en) ₃](SO ₄) | CuN ₆ | <i>P3/c</i> | 2.15 | | | <i>D₃(32)</i> site symmetry | ff |
| [Cu(OMPA) ₃](ClO ₄) ₂ | CuO ₆ | <i>P3c1</i> | 2.07 | | | <i>D₃(32)</i> site symmetry | gg |
| [Cu(IPCP) ₃](ClO ₄) ₂ | CuO ₆ | <i>C2/c</i> | 2.09 | | | No symmetry restrictions | hh |
| | | | Group E. Miscellaneous | | | | |
| CsCrCl ₃ | CrCl ₆ | <i>P6₃/mc</i> | 2.42 (three) | | | <i>C_{3v}</i> site symmetry, chain polymer | ii |
| | | | 2.62 (three) | | | | |

^a hfacac = hexafluoroacetylacetonate; en = ethylenediamine; pn = 1,2-propanediamine; bdanH = bis(dimethylamino)naphthalene hydride; dien = diethylenetriamine; OMPA = octamethylpyrophosphoramide; PCP = octamethylmethylenediphosphonic diamide; IPCP = tetraisopropylmethylendiphosphonate. ^b Nearly equivalent bond distances have been averaged. ^c S. Schneider and R. Hoppe, *Z. Anorg. Allg. Chem.*, **376**, 268 (1970). ^d D. R. Sears and J. L. Hoard, *J. Chem. Phys.*, **50**, 1066 (1969). ^e A. J. Edwards, *J. Chem. Soc. A*, 2653 (1971). ^f K. H. Jack and R. Maitland, *Proc. Chem. Soc., London*, 232 (1957). ^g J. W. Tracy, N. W. Gregory, E. C. Lingafelter, J. D. Dunitz, H.-C. Mez, R. E. Rundle, C. Scheringer, H. L. Yakel, Jr., and M. K. Wilkinson, *Acta Crystallogr.*, **14**, 927 (1961). ^h J. W. Tracy, N. W. Gregory, J. M. Stewart, and E. C. Lingafelter, *ibid.*, **15**, 460 (1962). ⁱ C. Billy and H. M. Haendler, *J. Amer. Chem. Soc.*, **79**, 1049 (1957). ^j N. C. Stephensen and D. P. Mellor, *Aust. J. Sci. Res., Ser. A*, **3**, 581 (1950). ^k A. F. Wells, *J. Chem. Soc.*, 1670 (1947). ^l L. Helmholz, *J. Amer. Chem. Soc.*, **69**, 886 (1947); A. W. Schlueter, R. A. Jacobson, and R. E. Rundle, *Inorg. Chem.*, **5**, 277 (1966); A. F. Wells, *J. Chem. Soc.*, 1662 (1947). ^m D. Babel, *Z. Anorg. Allg. Chem.*, **336**, 200 (1965); *Struct. Bonding*, **3**, 1 (1967). ⁿ I. Hjerten and B. Nyberg, *Acta Chem. Scand.*, **27**, 345 (1973). ^o B.-M. Anthl, B. K. S. Lundberg, and N. Ingri, *Acta Chem. Scand.*, **26**, 3984 (1972). ^p D. E. Fenton, M. R. Turner, and B. L. Vickery, *J. Chem. Soc. D*, 93 (1971); M. R. Truter and B. V. Vickery, *J. Chem. Soc., Dalton Trans.*, 395 (1972). ^q D. H. Templeton, S. Ray, and A. Zalkin, private communication. ^r T. Okamoto, K. Matsumoto, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **43**, 1915 (1970). ^s F. S. Stephensen, *J. Chem. Soc. A*, 2233 (1969). ^t A. F. Wells, "Structural Inorganic Chemistry," 3rd ed., Oxford University Press, Glasgow, 1962, p 877. ^u H. G. von Schnering, *Z. Anorg. Allg. Chem.*, **353**, 13 (1967). ^v K. Knox, *Acta Crystallogr.*, **30**, 991 (1959). ^w P. T. Miller, P. G. Lenhert, and M. D. Joesten, *Inorg. Chem.*, **11**, 2221 (1972). ^x F. S. Stephens, *J. Chem. Soc. A*, 883 (1969). ^y M. A. Hepworth and K. H. Jack, *Acta Crystallogr.*, **10**, 345 (1957). ^z A. Okazaki and Y. Suemune, *J. Phys. Soc. Jap.*, **16**, 176 (1961). ^{aa} P. M. Laugt, J. C. Guitel, I. Nordjman, and G. Bassi, *Acta Crystallogr., Sect. B*, **28**, 201 (1972). ^{bb} N. V. Mani and S. Rasasrshan, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **115**, 97 (1961). ^{cc} E. C. Lingafelter and H. Montgomery, *Proc. Int. Conf. Coord. Chem.*, **8**, 129 (1964). ^{dd} J. A. Bertrand and D. A. Carpenter, *Inorg. Chem.*, **5**, 514 (1966). ^{ee} D. L. Cullen and E. C. Lingafelter, *ibid.*, **10**, 1264 (1971). ^{ff} M. Cole, G. Guiseppe, and F. Mazzi, *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat., Natur.*, **96**, 381 (1962); D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, **9**, 1858 (1970). ^{gg} M. D. Joesten, M. S. Hussain, P. G. Lenhert, and J. H. Venables, *J. Amer. Chem. Soc.*, **90**, 5623 (1968). ^{hh} P. T. Miller, P. G. Lenhert, and M. D. Joesten, *Inorg. Chem.*, **12**, 218 (1973). ⁱⁱ G. L. McPherson, T. J. Kistenmacher, J. B. Folkers, and G. D. Stucky, *J. Chem. Phys.*, **57**, 3771 (1972).

Table XII. Crystal Field Calculation of the Jahn-Teller Distortion in $\text{Mn}(\text{acac})_3^a$

| Case no. | ϕ_2 | $q_1, \text{\AA}$ | $q_2, \text{\AA}$ | E_+, kK | E_-, kK | $\Delta E_{\text{JT}}, ^b \text{kK}$ | Characteristic |
|----------|------------------|-------------------|-------------------|------------------|------------------|--------------------------------------|--|
| 1 | $0, \pm 2\pi/3$ | -0.054 | +0.121 | 1.762 | -0.672 | 2.434 | Tetragonal compression, "through points" |
| 2 | $\pi, \pm \pi/3$ | -0.054 | -0.121 | | | | |
| 3 | $\pi, \pm \pi/3$ | -0.054 | +0.109 | 1.458 | -0.612 | 2.070 | Tetragonal elongation, "saddle points" |
| 4 | $0, \pm 2\pi/3$ | -0.054 | -0.109 | | | | |

^a The various calculated integrals are $B_2 = 0.3012 \text{ mdyne}$, $B_4 = 0.1840 \text{ mdyne}$, $\alpha = 0.3740 \text{ mdyne}$, $C_2 = -0.4820 \text{ mdyne/\AA}$, $C_4 = -0.3703 \text{ mdyne/\AA}$, and $\beta = -0.0909 \text{ mdyne/\AA}$ for $R_{\text{Mn-O}} = 1.985 \text{ \AA}$ (and $k_1 = k_2 = 1.69 \text{ mdyne/\AA}$). ^b The Jahn-Teller energy ΔE_{JT} is the difference between E_+ and E_- .

metry. This prevents a characterization of the distortion since molecular disordering about the high-symmetry axis also adequately interprets the data.

The origin of the particular distortion observed for various crystals of $\text{Mn}(\text{acac})_3$ remains obscure. Subtle effects of the packing forces are likely to be responsible, although these are not readily apparent from the unit cell data (Figure 4). Theoretical calculations for the isolated molecule assuming a crystal field model are also ambiguous, but the correct magnitude of the distortion³⁹ is obtained assuming reasonable force constants for the metal-ligand vibrations. The existence of two distinct Mn-O_6 geometries in crystalline⁶ manganese(III) tropolonate establishes the fact that energy differences between various forms of distortion in these potentially D_3 systems are very small. The ability of bis(hexafluoroacetylacetonato)bis(pyridine)zinc(II) with its "compressed octahedral" ZnO_4N_2 geometry to reduce the "axially elongated" tetragonality about Cu^{II} when bis(hexafluoroacetylacetonato)bis(pyridine)copper(II) is doped³⁷ into the zinc (based on paramagnetic resonance results) is further evidence pointing toward the conclusion that lattice forces have a more pronounced effect upon whether Jahn-Teller susceptible complexes are distorted in a compressed or elongated manner than do internal electronic forces within the molecules.

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Appendix

The G_k , B_k , and C_k Integrals for Double- ζ Type 3d Orbitals

The radial atomic function integrals used for the crystal field calculation of the Jahn-Teller distortion are defined as³⁵

$$G_k = \int_0^\infty R(r) \frac{r_{<}^k}{r_{>}^{k+1}} R(r) r^2 dr$$

$$B_k = dG_k/dr_0$$

$$G_k = d^2G_k/dr_0^2$$

where $R(r)$ is the radial portion of an atomic wave function and r is in atomic units. The metal-ligand distance is r_0 , and $r_{<}$ is the lesser value of r_0 and r , while $r_{>}$ is the greater value of r_0 and r . Using the definitions of $r_{<}$ and $r_{>}$, one can separate the G_k integral into two portions

$$G_k = \int_0^{r_0} R(r) \frac{r^k}{r_0^{k+1}} R'(r) r^2 dr + \int_{r_0}^\infty R(r) \frac{r_0^k}{r^{k+1}} R'(r) r^2 dr$$

The double- ζ type of 3d orbital is expressed as $R(r) = c_1 \chi_1 + c_2 \chi_2$. Substitution of the modified function into the G_k integral gives

(39) These calculations predict that the tetragonally elongated MnO_6 structure should have average dimensions of 2.026 and 1.932 \AA for the axial and equatorial Mn-O bonds, respectively. The dimensions established by Day²⁸ average 2.116 and 1.929 \AA , respectively, for the tetragonally elongated structure.

$$G_k = c_1^2 G_k(3d, 3d; \zeta_1, \zeta_1; r_0) + 2c_1 c_2 G_k(3d, 3d; \zeta_1, \zeta_2; r_0) + c_2^2 G_k(3d, 3d; \zeta_2, \zeta_2; r_0)$$

where

$$G_k(3d, 3d; \zeta_1, \zeta_2; r_0) = \int_0^\infty \chi_1 \frac{r_{<}^k}{r_{>}^{k+1}} \chi_2 r^2 dr =$$

$$\frac{1}{r_0^{k+1}} \int_0^{r_0} \chi_1 \chi_2 r^{k+2} dr + r_0^k \int_{r_0}^\infty \chi_1 \chi_2 r^{1-k} dr =$$

$$\frac{8}{45} (\zeta_1 \zeta_2)^{7/2} \left[\frac{1}{r_0^{k+1}} \int_0^{r_0} e^{-(\zeta_1 + \zeta_2) r} r^{k+6} dr + r_0^k \int_{r_0}^\infty e^{-(\zeta_1 + \zeta_2) r} r^{5-k} dr \right]$$

Let $\rho = r/r_0$. Then

$$G_k(3d, 3d; \zeta_1, \zeta_2; r_0) = \frac{8}{45} (\zeta_1 \zeta_2)^{7/2} r_0^6 \left[\int_0^\infty e^{-(\zeta_1 + \zeta_2) r_0 \rho} \rho^{k+6} d\rho - \int_1^\infty e^{-(\zeta_1 + \zeta_2) r_0 \rho} \rho^{5-k} d\rho \right]$$

The expression above contains the Γ integral and the so-called A integrals³⁴ ($A_k(p) = \int_1^\infty \exp(-pr) x^2 dx$). When appropriate substitution is made, the expression reduces to

$$G_k(3d, 3d; \zeta_1, \zeta_2; r_0) = \frac{8}{45} (\zeta_1 \zeta_2)^{7/2} \left[\frac{(k+6)!}{(\zeta_1 + \zeta_2)^{k+7} r_0^{k+1}} - r_0^6 A_{k+6}(\zeta_1 r_0 + \zeta_2 r_0) + r_0^6 A_{5-k}(\zeta_1 r_0 + \zeta_2 r_0) \right]$$

in atomic units (hartrees).

To obtain cgs units, one needs to multiply by $4.3598 \times 10^{-11} \text{ erg/hartree} (=219.475 \text{ kK/hartree})$.

The master formulas for B_k and C_k are deduced by taking the appropriate derivatives

$$B_k(3d, 3d; \zeta_1, \zeta_2; r_0) = \frac{8}{45} (\zeta_1 \zeta_2)^{7/2} \left[\frac{-(k+1)(k+6)!}{(\zeta_1 + \zeta_2)^{k+7} r_0^{k+2}} - 6r_0^5 (A_{k+6} - A_{5-k}) + r_0^6 (\zeta_1 + \zeta_2) (A_{k+7} - A_{6-k}) \right]$$

$$C_k(3d, 3d; \zeta_1, \zeta_2; r_0) = \frac{8}{45} (\zeta_1 \zeta_2)^{7/2} \left[\frac{(k+1)(k+2)(k+6)!}{(\zeta_1 + \zeta_2)^{k+7} r_0^{k+3}} - 30r_0^4 (A_{k+6} - A_{5-k}) + 12r_0^5 (\zeta_1 + \zeta_2) (A_{k+7} - A_{6-k}) - r_0^6 (\zeta_1 + \zeta_2)^2 (A_{k+8} - A_{7-k}) \right]$$

The units of B_k are hartrees/Bohr radius and of C_k are hartrees/(Bohr radius)². The respective cgs conversion factors are thus $8.23888 \times 10^{-3} \text{ dyn}$ and $1.55692 \times 10^6 \text{ dyn/cm}$.

If $\xi_1 = \xi_2$, these expressions reduce to those reported previously.³⁴

A Fortran IV computer program has been used to calculate the G_k , B_k , and C_k integrals for specified r_0 and radial functions (Slater or double- ξ type).

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1864.

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Stereochemistry of Low-Spin Cobalt Porphyrins. V. Molecular Stereochemistry of Nitro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(3,5-lutidine)cobalt(III)

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Nitro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(3,5-lutidine)cobalt(III) (I) is obtained by the oxidation of nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt in the presence of 3,5-lutidine. Crystals of I crystallize in the orthorhombic system, space group *Fdd2*. The unit cell has $a = 22.01$ (1) Å, $b = 34.29$ (2) Å, and $c = 10.884$ (6) Å and contains eight molecules. The molecule has a crystallographically imposed twofold axis of symmetry. The calculated and experimental densities are 1.33 and 1.30 g/cm³ at $20 \pm 1^\circ$. Diffracted intensities were recorded with graphite-monochromated Mo K α radiation on a computer-controlled diffractometer with θ - 2θ scanning. All independent reflections for $(\sin \theta)/\lambda \leq 0.742 \text{ \AA}^{-1}$ were measured; 3239 reflections were retained as observed. These data were employed for the determination of structure using the heavy-atom technique and least-squares refinement of the 272 structural parameters. The final conventional and weighted discrepancy factors are 0.045 and 0.059, respectively. The octahedral coordination group has an average equatorial Co-N_p distance of 1.954 Å; the axial bond to lutidine nitrogen is 2.036 (4) Å and to the nitro nitrogen is 1.948 (4) Å. The effect of the porphyrin conformation on the Co-N_p distances is discussed.

The earlier papers in this series have emphasized the importance and the origin of our interest in the stereochemistry of low-spin cobalt porphyrins.¹⁻⁴ In particular, our interest in nitrosylcobalt porphyrins has been detailed in our report on the molecular stereochemistry of nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt, ONCoTPP.¹ Our attempts to prepare crystals of a six-coordinate derivative, ONCoTPP(B), in which B is one of several amines, were frustrated by the facile decomposition of the desired nitrosyl complexes to other products. In the course of investigating the nature of these other products, we prepared single crystals of nitro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(3,5-lutidine)cobalt(III) *via* the conversion of coordinated nitric oxide to coordinated nitrite ion. We now report the quantitative stereochemistry of O₂N(3,5-lut)CoTPP. While this structure determination was in progress, a preliminary study of similar reactions of oxygen and cobalt nitrosyl complexes was reported.⁵

As we have emphasized elsewhere,^{1,6} the stereochemical parameters of the octahedral cobalt(III) porphyrins serve as useful standards of reference for the low-spin cobalt(II), iron(II), and iron(III) porphyrins. Furthermore, crystals of O₂N(3,5-lut)CoTPP would appear to provide an exceptionally convenient diamagnetic host for orientated single-crystal esr studies of paramagnetic nitrosyl metalloporphyrins. Finally, the structural parameters provide an (unanticipated)

test and confirmation of Hoard's⁷ recent treatment of the effects of porphinato skeletal ruffling on the metal-porphine nitrogen bond distances.

Experimental Section

Large single crystals of O₂N(3,5-lut)CoTPP were obtained by the slow evaporation (in air) of 1:1 chloroform-3,5-lutidine solutions of ONCoTPP.¹ Preliminary photographic examination established an orthorhombic unit cell with observed systematic absences of $h + k$, $k + l = 2n + 1$ for hkl , $k + l = 4n + 1$ for $0kl$, and $l + h = 4n + 1$ for $h0l$ which suggest the space group *Fdd2*.⁸ Lattice constants, $a = 22.01$ (1) Å, $b = 34.29$ (2) Å, and $c = 10.884$ (6) Å (λ 0.71069 Å), came from a least-squares refinement of the setting angles of 25 reflections, each collected at $\pm 2\theta$. These constants led to a calculated density at $20 \pm 1^\circ$ of 1.33 g/cm³ for eight molecules in the unit cell. The experimental density, measured by flotation, was 1.30 g/cm³. Thus the molecule has a crystallographically required twofold axis of symmetry.

Intensity data were measured on a Syntex P1 diffractometer with graphite-monochromated Mo K α radiation; the sample crystal had dimensions of 0.35 × 0.35 × 0.60 mm. All independent data for which $(\sin \theta)/\lambda \leq 0.742 \text{ \AA}^{-1}$ ($2\theta = 63.7^\circ$) were measured by θ - 2θ scanning. Variable scan rate techniques were employed;³ the base width of the scan was 1.0° at $2\theta = 0.0^\circ$ and background counts were taken at the extremes of the scan for a time equal to the time required for the scan itself. Four standard reflections were used for periodic checking (every 50 reflections) of the alignment and possible deterioration of the crystal; only small random variations in the intensities were noted. Data were processed as described previously³ and all data having $F_o > 2\sigma_{F_o}$ were taken as observed. A total of 3239 independent reflections, ~90% of the theoretical number possible, were retained and used for the determination and refinement of the structure. With the cited dimensions of the crystal and a linear absorption coefficient of 0.48 mm⁻¹ for Mo K α radiation, the maximum error in a structure amplitude occasioned by the neglect of absorption corrections was seen to be $\leq 2.5\%$.

(1) W. R. Scheidt and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8281 (1973).

(2) W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8289 (1973).

(3) W. R. Scheidt, *J. Amer. Chem. Soc.*, **96**, 84 (1974).

(4) W. R. Scheidt, *J. Amer. Chem. Soc.*, **96**, 90 (1974).

(5) S. G. Clarkson and F. Basolo, *J. Chem. Soc., Chem. Commun.*, **670** (1972); *Inorg. Chem.*, **12**, 1528 (1973).

(6) J. L. Hoard, *Science*, **174**, 1295 (1971).

(7) J. L. Hoard, *Ann. N. Y. Acad. Sci.*, **206**, 18 (1973).

(8) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1969, p 129.