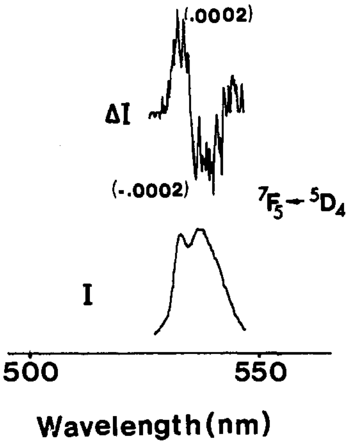


Figure 2. Total luminescence (*I*) and circularly polarized luminescence (Δ*I*) for a 1:5 mixture of Tb and racemic malic acid at a pH of 9.4. The values in parentheses are the measured luminescence dissymmetry ratios.

range of pH conditions. The formation constant (K_1)[18] of the complex has been reported to be ~5 × 10^8 and is, in fact, the largest value observed for this general type of ligand. The intensity of the luminescence and the sharpness of the observed transitions are consistent with this species being a very tight complex. The observation of CPL from the solution is consistent with D_3 geometry. The other possible nine-coordinate complex, in which the terdentate ligands occupy facial positions on the tricapped prism, has C_{3h} symmetry and, therefore, will exhibit no optical activity.

No CPL was detected from the 3:1 complex of $Tb(ODA)_3^{3-}$. This species also adopts the D_3 geometry in the crystal and has been presumed to have a similar geometry in aqueous solutions.[5,6] The sensitivity of our experimental apparatus under the conditions used here is such that the $|g_{lum}|$ values for this complex must be less than 1 × 10^{-4}, considerably smaller than that observed for the Tb–DPA system. The binding constant for Tb–ODA is ~2 × 10^5, much smaller than that for Tb–DPA. The absence of measurable differential emission intensity could be due to a small circular dichroism (CD), i.e. g_{abs} at 488 nm, or small values for g_{lum}, or a combination of the two. The measured CPL of the $Tb(ODA)_3^{3-}$ crystals is quite large.[10] It could be that the "looseness" of the complex in solution leads to a flexibility in the ligands that tend to average out the optical activity or the species may exist at least in some percentage as the C_{3h} isomer. Attempts at measuring Δ*I* using the much weaker 494-nm Ar ion laser line were unsuccessful. Similar attempts at measuring the CPL from solutions of $Tb(IDA)_3^{3-}$ using circularly polarized excitation were also unsuccessful. This species has been suggested to have C_{3h} geometry;[9] thus no CPL would be expected. The upper limit on the $|g_{lum}|$ value is again ~1 × 10^{-4}.

In Figure 2 is plotted the differential emission intensity for a 0.040 M solution of Tb(III) with excess racemic malic acid at a pH of 9.4. This system is an inherently more complicated one, since the optical activity that one observes may be due both to the configuration of the ligands around the central ion and to the chirality of the ligands themselves. In addition, this well-studied system has been shown to be very sensitive to pH, to exist as polymeric species at some pH values, and to include hydroxide ions in the coordination sphere at high pH.[19] Nevertheless, the kinds of results presented here may yield information concerning the optical activity of the emitting species and the nature of the equilibrium mixture that is not easily obtainable by other means.

The measurement of CPL from racemic solutions is a useful experimental probe, since one is able to examine the chiroptical properties of mixtures without having to resolve them. The results reported here indicate that the $Tb(DPA)_3^{3-}$ species probably exists as the D_3 isomer in aqueous solution. It should be possible to apply the theoretical approach of Richardson et al.[20] for the calculation of total and circular emission intensities to this system to see if there is agreement. A more detailed study of the Tb–IDA and Tb–ODA solution equilibrium is under way.

Registry No. $Tb(DPA)_3^{3-}$, 38682-37-0; $Tb(malate)_3^{3-}$, 96129-30-5.

---

(18) Martell, A. E. "Stability of Metal-Ion Complexes"; Chemical Society: London, 1971.

(19) See, for example: Brittain, H. G.; Richardson, F. S. *Inorg. Chem.* **1976**, *15*, 1507.

(20) Saxe, J. D.; Faulkner, T. R.; Richardson, F. S. *J. Chem. Phys.* **1982**, *76*, 1607.

Contribution from the Department of Chemistry,
Shizuoka University, Oya, Shizuoka 422, Japan

Crystal and Molecular Structure of Trimeric Bis(acetylacetonato)manganese(II)[1]

Shuzo Shibata,* Shigeki Onuma, and Hironao Inoue[2]

Received August 28, 1984

The molecular structures of anhydrous acetylacetonates of many bivalent first-row transition metals have been determined, and it has been found that the iron,[3,4] cobalt,[5] nickel,[6,7] and zinc[8] chelates are polymeric with structures formed by bridging by the oxygen atoms of the ligands, while the chromium[9] and copper[10] chelates are monomeric with planar structures in the solid phases. However, the structure of the manganese analogue, a well-known compound in the series, has remained undetermined until now. Graddon and Mockler[11] measured its molecular weight in benzene solution at various concentrations and reported that the manganese chelate is trimeric in the solution. They also suggested that the structure was similar to that of the corresponding nickel trimer, where NiO_6 octahedra are fused by sharing triangular faces, though most of the manganese(II) complexes so far studied have been found to be tetrahedral and octahedral for four- and six-coordination, respectively.[12] We now report the crystal and molecular structure of bis(acetylacetonato)manganese(II) and describe the coordination polyhedra of the complexes and the related structure of the acetylacetone ligands in detail.

Experimental Section

Bis(acetylacetonato)manganese(II) dihydrate, $Mn(acac)_2 \cdot 2H_2O$, was prepared by a known procedure.[13] The dihydrate was transferred into a glass tube and heated at 60 °C with phosphorus pentoxide; the anhydrous compound obtained was pale yellow, and crystals (irregular prism) suitable for X-ray work were prepared by repeated sublimation in vacuo, first at 140 °C and then at 190 °C. The complex was stored in vacuo after preparation. Anal. Calcd for $C_{10}H_{14}O_4Mn$: C, 47.45; H, 5.57. Found: C, 47.42; H, 5.63.

---

(1) Preliminary report: Shibata, S.; Onuma, S.; Inoue, H. *Chem. Lett.* **1984**, 485.

(2) Present address: Rigaku Denki Co., Matsubaracho, Akishima, Tokyo 196, Japan.

(3) Shibata, S.; Onuma, S.; Iwase, A.; Inoue, H. *Inorg. Chim. Acta* **1977**, *25*, 33.

(4) Cotton, F. A.; Rice, G. W. *Nouv. J. Chim.* **1977**, *1*, 301.

(5) Cotton, F. A.; Elder, R. C. *Inorg. Chem.* **1965**, *4*, 1145.

(6) Bullen, G. J.; Mason, R.; Pauling, P. *Inorg. Chem.* **1965**, *4*, 456.

(7) Hursthouse, M. B.; Laffey, M. A.; Moore, P. T.; New, D. B.; Raithby, P. R.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1982**, 307.

(8) Bennett, M. J.; Cotton, F. A.; Eiss, R. *Acta Crystallogr., Sect. B: Struct. Crsytallogr. Crsyt. Chem.* **1968**, *B24*, 904.

(9) Cotton, F. A.; Rice, C. E.; Rice, G. W. *Inorg. Chim. Acta* **1977**, *24*, 231.

(10) Starikova, Z. A.; Shugam, E. A. *Zh. Strukt. Khim.* **1969**, *10*, 290.

(11) Graddon, D. P.; Mockler, G. M. *Aust. J. Chem.* **1964**, *17*, 1119.

(12) Stephens, F. S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 3492.

(13) *Inorg. Synth.* **1960**, *6*, 164.

Table I. Fractional Coordinates (×10^4, for Mn ×10^5) and Equivalent Thermal Factors (Å^2)

	x	y	z	B_{eqv}
Mn(1)	28858 (9)	−24261 (11)	19522 (9)	2.5
Mn(2)	0	0	0	2.7
O(11)	4694 (3)	−1718 (4)	3106 (3)	3.6
O(12)	2017 (3)	305 (4)	1375 (3)	3.4
O(21)	4014 (3)	−4887 (4)	1274 (3)	3.7
O(22)	1445 (3)	−2536 (4)	−364 (3)	3.4
O(31)	3214 (3)	−3510 (4)	3648 (3)	3.5
O(32)	707 (3)	−1317 (4)	1814 (3)	3.4
C(11)	6459 (5)	−451 (8)	4191 (6)	4.6
C(12)	4963 (5)	−358 (6)	3273 (5)	3.3
C(13)	3969 (5)	1239 (6)	2659 (6)	3.8
C(14)	2587 (5)	1480 (6)	1755 (5)	3.4
C(15)	1668 (6)	3243 (7)	1157 (7)	5.2
C(21)	4951 (6)	−7558 (7)	132 (6)	4.7
C(22)	3852 (5)	−5780 (6)	113 (5)	3.4
C(23)	2697 (5)	−5243 (6)	−1191 (5)	3.7
C(24)	1585 (5)	−3718 (6)	−1355 (5)	3.3
C(25)	420 (6)	−3369 (8)	−2833 (6)	5.3
C(31)	3176 (7)	−4473 (9)	5437 (7)	5.9
C(32)	2488 (5)	−3446 (6)	4196 (5)	3.2
C(33)	1014 (5)	−2439 (6)	3725 (5)	3.5
C(34)	238 (5)	−1487 (6)	2578 (5)	3.3
C(35)	−1318 (5)	−543 (8)	2195 (6)	5.1

Cell parameters were estimated from Weissenberg photographs and refined by a least-squares method on the basis of 20 2θ values ($28 < 2\theta < 40°$), obtained on a Rigaku automated four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.709 26 Å), to a = 11.680 (6) Å, b = 8.429 (3) Å, c = 10.975 (5) Å, α = 106.24 (4)°, β = 119.54 (4)°, γ = 65.10 (3)°, and V = 849.1 (7) Å^3. The unit cell contains one trimer, $[Mn(acac)_2]_3$, mol wt = 759.48; D(calcd) = 1.45 g cm^{-3}. The space group $P\bar{1}$ was assumed and verified later by the successful structure refinement. Intensity measurements were carried out to 2θ = 50° by the ω–2θ scan technique for octants ($\pm h,\pm k,+l$) at room temperature. Approximate dimensions of the crystal used for X-ray work were 0.5 × 0.4 × 0.4 mm^3. Intensities of 3651 reflections were measured with a scan speed of 3° min^{-1} (ω) for the initial 1648 reflections and 6° min^{-1} (ω) for the remaining 2003 reflections, because of limited machine time available for this work. Three check reflections were monitored every 100 reflections. They showed a random fluctuation as $0.995 < [(\sum|F_o|/|F_o|_{initial})/3] < 1.007$. The intensities were corrected for Lorentz and polarization effects but not for absorption effects (μ = 11.1 cm^{-1}). The number of reflections with $|F_o| > 3\sigma(|F_o|)$ was 2565, and these were used in the subsequent structure refinement.

The structure of the centrosymmetric trimer was solved by the heavy-atom method: the position of a manganese atom was chosen at the origin of the unit cell, and the other non-hydrogen atoms could be easily located. The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined by a block-diagonal least-squares procedure using the UNICS III computation program system:[14] $\sum w||F_o| - |F_c||^2$ minimized, where $w = \sigma^{-2}(|F_o|)$; final R = 0.052 and R_w = 0.072; $(\Delta/\sigma)_{max}$ = 0.71; complex neutral-atom scattering factors from ref 15; hydrogen atoms ignored; final atomic parameters listed in Table I. Observed and calculated structure factors and anisotropic temperature factors are given in the supplementary material.

Results

The crystal of bis(acetylacetonato)manganese(II) is centrosymmetric, and its molecular structure is shown in Figure 1. Selected interatomic distances and angles are listed in Table II. Each manganese atom in the trimer is surrounded by six oxygen atoms, and one of the oxygen atoms of each ligand, O(j2), bridges the central and terminal manganese atoms. The coordination polyhedron of the terminal MnO_6 unit can be described as a near trigonal prism while that of the central one is a near octahedron (trigonal antiprism), and they are fused to yield a trimer by sharing triangular faces of oxygen atoms. The average O–O distance of the common triangular faces is 2.713 [7] Å, that of the outer triangular faces is 3.009 [26] Å, and both faces are separated by 2.790 [4] Å. The inner triangular faces are separated by 3.00 Å.

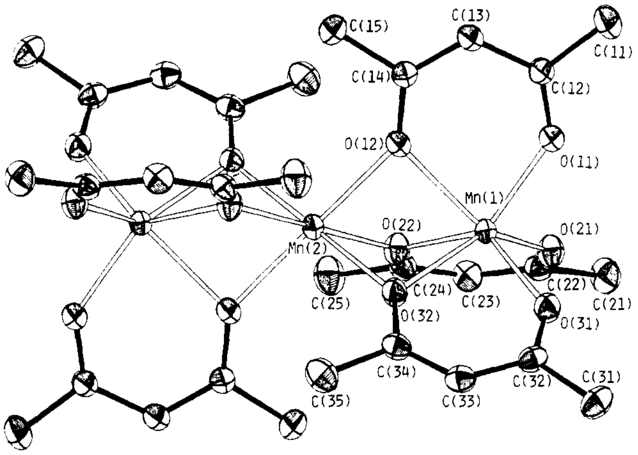


Figure 1. ORTEP drawing of $[Mn(acac)_2]_3$.

Table II. Bond Lengths and Bond Angles with Their Standard Deviations

(a) Bond Lengths (Å)

Mn(1)–Mn(2) 3.108 (2)

	j			
	1	2	3	av[a]
Mn(1)–O(j1)	2.103 (4)	2.096 (3)	2.097 (5)	2.099 [2]
Mn(1)–O(j2)	2.225 (4)	2.254 (3)	2.252 (4)	2.244 [9]
Mn(2)–O(j2)	2.163 (4)	2.175 (3)	2.171 (4)	2.170 [4]
O(j1)–C(j2)	1.252 (8)	1.254 (6)	1.238 (9)	1.248 [5]
O(j2)–C(j4)	1.283 (7)	1.279 (6)	1.271 (9)	1.278 [4]
C(j1)–C(j2)	1.506 (7)	1.504 (6)	1.499 (9)	1.503 [2]
C(j2)–C(j3)	1.430 (7)	1.421 (6)	1.444 (7)	1.432 [7]
C(j3)–C(j4)	1.374 (7)	1.365 (6)	1.371 (7)	1.370 [3]
C(j4)–C(j5)	1.517 (7)	1.523 (6)	1.526 (7)	1.522 [3]
O(j1)–O(j2)	2.785 (4)	2.798 (4)	2.787 (4)	2.790 [4]

	j, k			
	1, 2	1, 3	2, 3	av
O(j1)–O(k1)	3.004 (5)	3.057 (7)	2.967 (6)	3.009 [26]
O(j2)–O(k2)	2.713 (4)	2.701 (7)	2.724 (6)	2.713 [7]
O(j2)–O(k2)[b]	3.385 (5)	3.390 (5)	3.386 (5)	3.387 [2]

(b) Bond Angles (deg)

	j			
	1	2	3	av
O(j1)–Mn(1)–O(j2)	80.1 (1)	80.0 (1)	79.6 (2)	79.9 [2]
Mn(1)–O(j1)–C(j2)	134.8 (3)	135.3 (3)	136.2 (3)	135.4 [4]
Mn(1)–O(j2)–C(j4)	131.2 (2)	129.9 (2)	130.4 (3)	130.5 [4]
O(j1)–C(j2)–C(j3)	125.1 (5)	124.5 (5)	124.4 (5)	124.7 [2]
O(j2)–C(j4)–C(j3)	124.6 (6)	125.1 (6)	125.5 (5)	125.1 [3]
C(j2)–C(j3)–C(j4)	124.2 (6)	125.2 (6)	123.9 (5)	124.4 [4]
C(j1)–C(j2)–C(j3)	118.3 (6)	118.7 (5)	117.4 (5)	118.1 [4]
C(j3)–C(j4)–C(j5)	118.1 (6)	118.1 (6)	117.2 (5)	117.8 [3]
O(j1)–C(j2)–C(j1)	116.7 (5)	116.8 (5)	118.1 (5)	117.2 [5]
O(j2)–C(j4)–C(j5)	117.3 (5)	116.8 (5)	117.3 (5)	117.1 [2]

	j, k			
	1, 2	1, 3	2, 3	av
O(j1)–Mn(1)–O(k1)	91.3 (2)	93.4 (2)	90.1 (2)	91.6 [10]
O(j2)–Mn(1)–O(k2)	74.5 (1)	74.2 (1)	74.4 (1)	74.4 [1]
O(j2)–Mn(2)–O(k2)	77.4 (1)	77.1 (1)	77.6 (1)	77.4 [1]

[a] Parentheses indicate the esd of each value; brackets indicate $[\sum\Delta_i^2/(n(n-1))]^{1/2}$ for three values whose unweighted arithmetic average is given. [b] Symmetry operation $-x, -y, -z$.

In the terminal unit, the average O–Mn–O bite angle is 79.9 [2]°, the average O(j1)–Mn(1)–O(k1) is 91.6 [10]°, and the average O(j2)–Mn(1)–O(k2) is 74.4 [1]°. This distorted-trigonal-prismatic arrangement of oxygen atoms around the manganese atom is remarkably diffferent from that in the nickel trimer, where

---

(14) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69. Johnson, C. K. *Oak Ridge Natl. Lab.*, [*Rep.*] *ORNL* (*U.S.*) **1965**, *ORNL-3794*.

(15) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

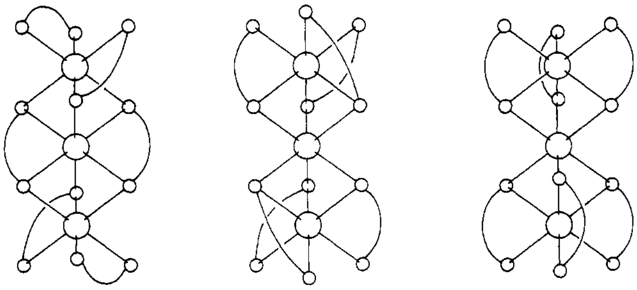


Figure 2. Schematic drawings of the coordination in $[Ni(acac)_2]_3$, $[Co(OCH_2CH_2NH_2)_2]_3{}^{2+}$, and $[Mn(acac)_2]_3$ chelates.

all the coordination polyhedra of the three nickel atoms were described as octahedra, shown in Figure 2.

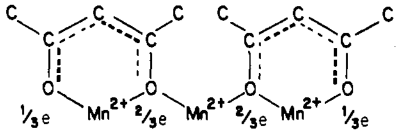
The average Mn–O distance in the central MnO_6 unit is 2.170 [4] Å, while the six Mn–O distances in the terminal MnO_6 unit are grouped into two classes with averages Mn(1)–O(*j*1) = 2.099 [2] Å and Mn(1)–O(*j*2) = 2.244 [9] Å; thus the Mn–O(bridging) distances are 0.145 Å longer than the Mn–O(nonbridging) distance. This large difference indicates that each of the ligands in this compound coordinates the Mn atom unsymmetrically.

The three independent ligand molecules are planar; deviations of the atoms from the least-squares mean planes are given in the supplementary material. The average angle between the mean planes is 120.0 [4]°. Corresponding bond distances and angles within the three ligands are very similar; however, the average distances noticed for C–O(nonbridging) and C–O(bridging) are 1.248 [5] and 1.278 [4] Å, respectively, and the average endocyclic C–C bond distance adjacent to the C–O(nonbridging) bond is 1.432 [7] Å and adjacent to the C–O(bridging) bond is 1.370 [3] Å. The differences are significant as compared with individual esd's. Associated with the discrepancies in distances mentioned above, two average angles of Mn–O–C, 130.5 [4] and 135.4 [4]°, are also found in Table II.

Discussion

As is well-known, many of the acetylacetone complexes of the first-row transition metals are polymeric, and now bis(acetylacetonato)manganese(II) has also been found to be trimeric, as is the nickel complex. It is very interesting that this chelate involves a trigonal-prismatic structure as D_{3h}–O_h–D_{3h} in contrast with O_h–O_h–O_h for the nickel complex as shown in Figure 2. A trigonal prism is predicted to be less stable than an octahedron because of the closer contacts between the six donor atoms. But this structure may be favored if chelates have large metal–ligand atom distances and small bite angles.

The first report of a trigonal-prismatic structure was on $Re(S_2C_2Ph_2)_3$[16] and $Mo(S_2C_2H_2)_3$[17] chelates. This structure was also revealed in tris(dipivaloylmethanate)erbium,[18] in which the oxygen atoms, instead of the sulfur atoms, coordinate the central atom. Polynuclear complexes containing trigonal-prismatic units were found in $[Co(Co(OCH_2CH_2NH_2)_3)_2]^{2+}$, which is described as O_h–D_{3h}–O_h with the central cation of Co(II).[19] But in the central unit the metal is not chelated by the ligands. Thus trimeric $Mn(acac)_2$ is really the first example of a neutral chelate including trigonal-prismatic units, in which the metals are coordinated to the ligands, indicated as $[Mn(Mn(acac)_3)_2]$. The occurrence of the trigonal-prismatic structure may be due to less repulsive interaction between the neighboring oxygen atoms because of the rather small O–Mn–O bite angles with the large Mn–O distances. Of course, the octahedral structure of the central unit is understandable by considering the large repulsions between the methyl groups in the terminal ligands. Another special feature in the results of the trimeric $Mn(acac)_2$ is that the structure of the acetylacetone ligand is not symmetric. In monomeric chelates their structures should be symmetric[20] because the acac ligands resonate completely. However, in the trimeric $Mn(acac)_2$ chelate the formula



with unsymmetric formal charges on the ligand atoms, i.e., $^1/_3$ e and $^2/_3$ e on the nonbridging and bridging atoms, respectively, is expected if we assume the same oxidation states of three manganese ions and completely ionic bonding of Mn–O. Accordingly, the ligand resonates incompletely, as illustrated, yielding an unsymmetric structure with two different bond orders for C–O and C–C in agreement with their experimental bond distances. Such deformed structures of acac ligands are very common but have not been documented until now in spite of the reports on many of the polymeric acac chelates.[3-8]

Registry No. $Mn(acac)_2{\cdot}2H_2O$, 14024-80-7; $[Mn(acac)_2]_3$, 95978-22-6.

Supplementary Material Available: Listings of anisotropic thermal parameters for non-hydrogen atoms, observed and calculated structure factors, and deviations of atoms from the least-squares planes (28 pages). Ordering information is given on any current masthead page.

---

(16) Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* **1966**, *5*, 411.

(17) Smith, A. E.; Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *J. Am. Chem. Soc.* **1965**, *87*, 5798.

(18) de Villiers, J. P. R.; Boeyens, J. C. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 2335.

(19) Bertrand, J. A.; Kelly, J. A.; Vassian, E. G. *J. Am. Chem. Soc.* **1969**, *91*, 2394.

(20) Lingafelter, E. C.; Braun, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 2951.

Contribution from the Chemistry Department,
Manchester University, Manchester M13 9PL, U.K.,
and Institute for Inorganic Chemistry,
D-3400 Göttingen, Federal Republic of Germany

Isolation and Crystal Structure of the Cubane-like Cluster $[Cr_4(OH)_4(mhp)_8]$ (mhp = 6-Methyl-2-hydroxypyridinate)

Lalarukh Akhter,[1a] William Clegg,*[1b] David Collison,[1a] and C. David Garner*[1a]

Received February 9, 1984

The mhp anion (Hmhp = 6-methyl-2-hydroxypyridine) has been shown in recent years to be versatile in its modes of binding to metal centers. In complexes $[M_2(mhp)_4]$, where M = Cr,[2,3] Mo,[2,4] W,[2] Ru,[5] Rh,[2,6,7] or Pd,[8] four mhp ligands bridge a pair of metal atoms in an arrangement with essentially D_{2d} symmetry, each metal atom bonding to two nitrogen and two oxygen atoms. The metal–metal separations in these complexes are among the shortest ever observed for each metal, although formal bond orders range from 4 (Cr, Mo, W) down to 0 (Pd). A different ar-

---

(1) (a) Manchester University. (b) Göttingen University. Present address: Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU, England.

(2) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

(3) Mitschler, A.; Rees, B.; Wiest, B.; Benard, M. *J. Am. Chem. Soc.* **1982**, *104*, 7501.

(4) Clegg. W.; Garner, C. D.; Akhter, L.; Al-Samman, M. H. *Inorg. Chem.* **1983**, *22*, 2466.

(5) (a) Berry, M.; Garner, C. D.; Hillier, I. H.; MacDowell, A. A.; Clegg, W. *Inorg. Chim. Acta* **1981**, *53*, L61. (b) Clegg, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 3112.

(6) (a) Berry, M.; Garner, C. D.; Hillier, I. H.; Macdowell, A. A.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1980**, 494. (b) Clegg, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2437.

(7) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 584.

(8) Clegg, W.; Garner, C. D.; Al-Samman, M. H. *Inorg. Chem.* **1982**, *21*, 1897.

0020-1669/85/1324-1725$01.50/0