Carbon Compounds of the Transition Metals. Part XXVIII.[1] Crystal Structure of Bromotriscarbonyl(phenyl isocyanide)manganese(I)

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The crystal structure of the title compound has been determined from 555 visually estimated *X*-ray reflexions and refined by least-squares techniques to *R* 11·1. Crystals are monoclinic, space group $P2_1/n$, with $a = 18{\cdot}03$, $b = 5{\cdot}93$, $c = 16{\cdot}83$ Å, $\beta = 107{\cdot}33°$, and $Z = 4$. The co-ordination about the manganese is close to regular octahedral with the two isonitrile groups mutually *cis* and the bromine *trans* to a carbonyl group. The groups Mn–C–O and Mn–C–N–Ph are linear. Mean bond lengths are: Mn–Br 2·527(8), Mn–CO 1·74(3), Mn–CN 1·92(3), C–O 1·17(3), and C–N 1·12(3) Å.

ALTHOUGH close correspondence in the structural behaviour of carbonyl and isonitrile ligands may occur in metal complexes, a complete parallelism is not to be expected since isonitriles appear to be stronger sigma donors than carbonyl.[2] Nevertheless, in the reported structure of *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNPh)$, in which the isonitrile group occurs as a bridging group between the iron atoms,[3] the Fe–CN distances are the same as the Fe–CO(br) values, 1·90 Å.

Other structural data on isonitrile complexes are rather sparse. The Fe–C distance reported from the ion $(MeNC)_6Fe^{2+}$ is 1·85 Å,[4a] and from β-tetramethylferrocyanide is 1·8 Å,[4b] both of which are longer than most Fe–CO distances, but it is difficult to estimate the reliability of these values since the work refers to two-dimensional *X*-ray analyses. More recently the structure of $[(MeNC)_5Co]_2{}^{4+}$ was reported[5] with Co–CN distances 1·88(4) Å. This value again seems somewhat larger than those reported for Co–CO distances, around 1·80 Å,[6,7] but even here the difference is barely significant, particularly since the high thermal vibration of the atoms severely limited the precision with which the isonitrile ligands could be located.

We have studied the structure of bromotriscarbonylbis(phenyl isocyanide)manganese in an attempt to resolve

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[1] Part XXVII, D. Bright and O. S. Mills, *J.C.S. Dalton*, 1972, 2465.

[2] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 712.

[3] K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Comm.*, 1965, 181.

[4] (*a*) H. M. Powell and G. W. R. Bartindale, *J. Chem. Soc.*, 1945, 799; (*b*) R. Hulme and H. M. Powell, *ibid.*, 1957, 719.

[5] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 1495.

[6] P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 261.

[7] G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, 1964, **17**, 732.

this problem since both types of linkage occur within the same molecule which therefore affords a direct comparison of metal–carbon distances.

EXPERIMENTAL

A number of carbonyl(isonitrile)metal complexes were prepared but only two [the present complex and nonacarbonyl(phenyl isocyanide)dimanganese] * yielded crystals suitable for *X*-ray examination. Both gave crystals of low quality but those of the bromo-derivative appeared marginally better and were chosen for the analysis.

Crystal Data.—$C_{17}H_{10}BrMnN_2O_3$, $M = 425{\cdot}1$, Monoclinic, $a = 18{\cdot}03$, $b = 5{\cdot}93$, $c = 16{\cdot}83$ (all $\pm 0{\cdot}05$) Å, $\beta = 107{\cdot}33°$, $D_m = 1{\cdot}62$, $Z = 4$, $D_c = 1{\cdot}64$. Space group $P2_1/n$ by systematic absences. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 96·3 cm^{-1}.

One of the better crystals, with dimensions *ca.* 0·3 × 0·1 × 0·005 mm was selected and photographs of the layers *h*0—3*l* taken by Weissenberg geometry with Cu-K_α radiation and multiple-film packs. Data were estimated visually and gave 555 reflexions. Data about axes other than *b* could not be obtained owing to the crystal shape. Precession photographs, whether taken with Cu or Mo radiation, showed too few reflexions for reliable interlevel scale factors between the Weissenberg layers. Scale factors were therefore initially calculated from exposure times and finally determined by least-squares refinement in the later stages of the structure analysis. Lorentz and polarisation corrections were applied to the data but no attempt was made to apply absorption corrections.

Structure Determination and Refinement.—The co-ordinates of the two heavy atoms were determined from the three-dimensional Patterson function but errors in the initial inter-level scale factors were sufficient to make impossible a decision as to which site was occupied by manganese and which by bromine based on peak height. The initial assumption made was to place two manganese atoms at these sites and to proceed by difference-Fourier series. These syntheses served to locate the light atoms and the heavy-atom site occupancy was then clear from the stereochemistry.

The structure was refined by full-matrix least-squares methods in which the function minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/F_o^2$. The effects of anomalous scattering by manganese and bromine were allowed for in the structure-factor calculations [8] by use of the values of $\Delta f'$ and $\Delta f''$ listed in ref. 9. Remaining scattering-factor values were taken from ref. 10. In view of the low quality of the reflexion data, the phenyl rings were refined as rigid groups [11] with C–C 1·39 Å. Least-squares refinement, with allowance for isotropic motions only, converged at *R* 11·1% and a difference Fourier synthesis then showed no features >0·9 eÅ^{-3}. Final atom parameters from this cycle, together with those derived from the rigid-body parameters, are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20859 (10 pp., 1 microfiche).†

DISCUSSION

Figures 1(a) and (b) show the structure when projected along the *b* and *c* axes. A schematic view of the molecule, with the atom-numbering scheme used, is shown in Figure 2. Bond lengths and angles, with standard deviations, are listed in Tables 2 and 3.

TABLE 1

Atomic parameters

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å^2
Mn	0·1057(3)	0·111(2)	0·3149(4)	3·3(2)
Br	−0·0094(3)	−0·114(1)	0·2296(3)	4·1(2)
C(1)	0·183(3)	0·277(10)	0·369(3)	4·3(11)
O(1)	0·232(2)	0·392(7)	0·414(2)	6·3(9)
C(2)	0·107(3)	−0·057(12)	0·400(4)	7·2(15)
O(2)	0·105(2)	−0·171(7)	0·454(2)	7·1(9)
C(3)	0·172(2)	−0·069(9)	0·287(2)	2·3(8)
O(3)	0·208(2)	−0·208(7)	0·266(2)	5·9(9)
C(4)	0·102(2)	0·278(8)	0·216(2)	2·2(8)
N(1)	0·103(2)	0·373(6)	0·159(2)	2·7(7)
C(5)	0·028(2)	0·298(8)	0·340(2)	2·0(8)
N(2)	−0·023(2)	0·389(7)	0·350(2)	3·7(8)
C(A1)	0·108(2)	0·484(5)	0·088(1)	1·4(8)
C(A2)	0·141(2)	0·347(4)	0·040(2)	2·6(11)
C(A3)	0·139(2)	0·414(5)	−0·039(2)	3·4(10)
C(A4)	0·105(2)	0·618(6)	−0·071(1)	4·3(11)
C(A5)	0·072(2)	0·755(4)	−0·024(2)	3·6(10)
C(A6)	0·074(2)	0·688(5)	0·056(2)	4·8(8)
C(B1)	−0·095(1)	0·446(8)	0·356(2)	5·0(12)
C(B2)	−0·110(2)	0·645(7)	0·392(2)	6·1(13)
C(B3)	−0·184(2)	0·687(6)	0·397(2)	7·4(19)
C(B4)	−0·243(2)	0·530(8)	0·366(3)	8·8(18)
C(B5)	−0·228(2)	0·332(7)	0·330(2)	9·3(15)
C(B6)	−0·154(2)	0·289(6)	0·325(2)	5·6(13)

TABLE 2

Bond distances (Å)

Mn–Br	2·527(8)	C(1)–O(1)	1·19(5)
Mn–C(1)	1·73(5)	C(2)–O(2)	1·15(6)
Mn–C(2)	1·73(7)	C(3)–O(3)	1·17(5)
Mn–C(3)	1·77(5)	C(4)–N(1)	1·12(4)
Mn–C(4)	1·92(4)	C(5)–N(2)	1·12(4)
Mn–C(5)	1·93(4)	N(1)–C(A1)	1·39(8)
		N(2)–C(B1)	1·38(9)

TABLE 3

Bond angles (°)

Br–Mn–C(1)	177(2)	C(3)–Mn–C(5)	176(2)
Br–Mn–C(2)	88(2)	C(4)–Mn–C(5)	93(2)
Br–Mn–C(3)	92(2)	Mn–C(1)–O(1)	171(4)
Br–Mn–C(4)	88(1)	Mn–C(2)–O(2)	177(5)
Br–Mn–C(5)	84(1)	Mn–C(3)–O(3)	172(4)
C(1)–Mn–C(2)	95(3)	Mn–C(4)–N(1)	176(3)
C(1)–Mn–C(3)	89(2)	Mn–C(5)–N(2)	172(3)
C(1)–Mn–C(4)	89(2)	C(4)–N(1)–C(A1)	178(5)
C(1)–Mn–C(5)	95(2)	C(5)–N(2)–C(B1)	164(6)
C(2)–Mn–C(3)	92(2)	N(1)–C(A1)–C(A2)	111(7)
C(2)–Mn–C(4)	176(2)	N(1)–C(A1)–C(A6)	128(7)
C(2)–Mn–C(5)	89(2)	N(2)–C(B1)–C(B6)	116(9)
C(3)–Mn–C(4)	86(2)	N(2)–C(B1)–C(B2)	124(9)

The crystal structure consists of individual molecules of (I), $MnBr(CO)_3(CNPh)_2$. The shortest intermolecular

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* *Crystal Data*.—$C_{16}H_5NO_9Mn_2$, $M = 465{\cdot}1$, nonacarbonyl(phenyl isocyanide)dimanganese, Monoclinic, $a = 12{\cdot}32$, $b = 9{\cdot}17$, $c = 17{\cdot}88$ Å, $\beta = 108{\cdot}3°$, $D_m = 1{\cdot}59$, $D_c = 1{\cdot}61$ for $Z = 4$, space group $P2_1/c$ by systematic absences.

† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[8] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, 1964, **17**, 781.

[9] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[10] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[11] S. J. La Placa and J. A. Ibers, *Acta Cryst.*, 1965, **18**, 511.

distance, excluding hydrogen contacts, is N(1) · · · O(3) 3·29 Å. The co-ordination about the metal atom is close to regular octahedral; the two isonitrile ligands are mutually *cis* and the bromine atom *trans* to a carbonyl group.

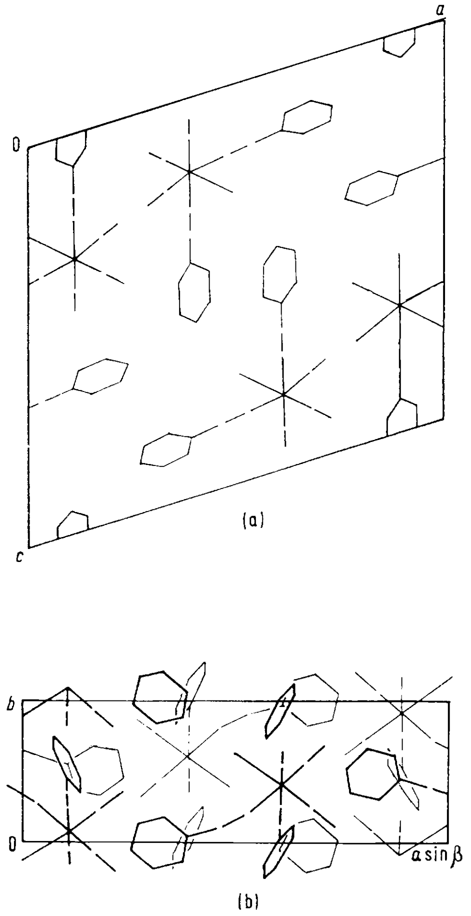

FIGURE 1 Packing diagrams projected (a) along *b* and (b) along *c*

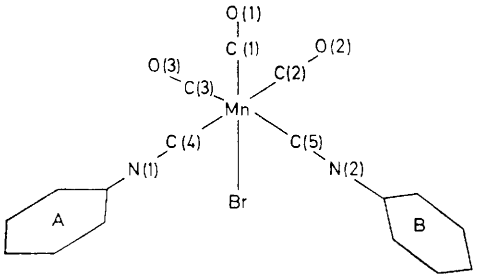

FIGURE 2 Schematic diagram showing atom numbering scheme

The Mn–Br distance [2·527(8) Å] is in excellent agreement with the mean of the Mn–Br distances found in $[Br(CO)_4Mn]_2$ [2·526(5) Å].[12] It might have been argued that a shorter distance is expected in (I) because the bromine is terminal, whereas it bridges in the dimer. However, it has been shown from a study of octahedral nitrogen-metal complexes,[13] that when a molecule contains a mixture of strongly bonding ligands, *e.g.* nitrido, carbonyl, *etc.*, together with weakly bonding ligands, *e.g.* halogen, the bond lengths observed for the weakly co-ordinating ligands are largely controlled by the intramolecular non-bonding interactions. That these factors operate in the manganese–carbonyl–bromine system is shown by the agreement of the non-bonding nearest-neighbour Br · · · C distances. In (I) these range from 3·01 to 3·13 (mean 3·07) and in the dimer from 3·04 to 3·18 (mean 3·12 Å).

In common with the previous studies of compounds with terminally co-ordinated isonitrile ligands,[4,5,14] the precision with which the geometry of the molecule has been determined leaves more to be desired. Nevertheless, in spite of the high standard deviations, the agreement between chemically similar bond lengths in the molecule is quite good, and the mean Mn–CN distance [1·92(3) Å] is significantly longer than the mean Mn–CO distance [1·74(3) Å]. Thus it appears that the metal–isonitrile bonds are weaker than the metal–carbonyl bonds.

These observations are in conflict with the equality of distances[3] reported for the bridging isonitrile complex $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNPh)$ and it follows that the two modes of co-ordination are probably different. An alternative structure representation of the isonitrile molecule is the non-linear form, $R\diagup\ddot{N}{=}C\colon$, contribution from which is almost absent in the free ligand. However, this form could well participate as a major form in bridging co-ordination, acting as a ketimine. This view is in accord with the observed bond angle in the bridging isonitrile, the C–N–C angle is 131(2)°, close to the value of 120° expected for the ketimine group. In the case of terminally co-ordinated isonitrile groups, with one exception,[14] the arrangement M–C–N–C has been found to be linear or with small variation from linearity. In the present structure the angles found are C(4)–N(1)–C(A1) 178(5) and C(5)–N(2)–C(B1) 164(6)°, and bearing in mind the large standard deviation associated with the latter, even these values are scarcely significant. There is no evidence that the M–C–O and M–C–N–Ph groups are other than linear.

The occurrence of bridging isonitrile ligands is thus dependent upon the realisation of conditions which result in destabilisation of the otherwise energetically favourable linear form into a non-linear arrangement. It is thus probable that these are rare. From this viewpoint, linear triply bridging isonitrile groups, analogous to the triply bridging carbonyls found, *e.g.* in

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[12] L. F. Dahl and C-H. Wei, *Acta Cryst.*, 1963, **16**, 611.

[13] D. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 709.

[14] J. B. Wilford, N. O. Smith, and H. M. Powell, *J. Chem. Soc.* (*A*), 1968, 1544.

$(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$[15] and $Rh_6(CO)_{16}$,[16] may become more common than the doubly bridging variety although, as yet, no report of this mode of bonding has been made.

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[15] A. A. Hock and O. S. Mills, ' Advances in the Chemistry of the Co-ordination Compounds,' MacMillan, London, 1961, p. 640.

[16] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.