Journal of Organometallic Chemistry, 206 (1981) 177—184
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

π-COMPLEXES AS LIGANDS IN TRANSITION METAL COMPOUNDS

V *. INTERACTION OF π-PYRROLYLTRICARBONYLMANGANESE WITH PICRIC ACID

V.G. ANDRIANOV, Yu.T. STRUCHKOV, N.I. PYSHNOGRAEVA, V.N. SETKINA * and D.N. KURSANOV

Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Vavilov st. 28, Moscow (U.S.S.R.)

(Received August 14th, 1980)

Summary

It has been found that interaction of π-pyrrolyltricarbonylmanganese (PTM) with picric acid gives the binuclear complex I in which the central manganese atom is coordinated with three CO ligands, a PTM molecule, and a picrate anion; the latter two acting as two- and three-electron ligands, respectively.

Introduction

We have studied the interaction of π-pyrrolyltricarbonylmanganese (PTM) with trifluoroacetic acid using spectral methods (IR and ^{13}C and ^{1}H NMR), and concluded that both the manganese atom and the nitrogen atom of PTM can participate in protonation [1]. However, no complete agreement between the data from these methods was observed.

To establish the site of protonation of PTM, we tried to prepare a crystalline product from the interaction of PTM with a protic acid in order to determine its structure by X-ray diffraction. We have studied the interaction of PTM with several acids (CF_3COOH, H_3PO_4, HBF_4, and picric acid). Only in the case of picric acid did we succeed in isolating a crystalline compound suitable for X-ray diffraction analysis.

Results and discussion

The X-ray diffraction analysis of the product obtained shows that the interaction of PTM with piric acid in CH_2Cl_2 gives the binuclear complex I, instead

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* For part IV see ref. 5.

TABLE 1

ATOMIC COORDINATES (X 10^4) AND PARAMETERS OF TEMPERATURE FACTORS

Atom	x	y	z	B_{11} [a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(11)	5969(1)	3143(1)	3173(3)	1.84(9)	3.0(1)	1.3(1)	−0.69(8)	0.18(8)	−0.67(9)
Mn(12)	7884(1)	2945(1)	479(3)	2.03(9)	2.12(9)	2.0(1)	−0.59(8)	0.15(8)	−0.50(8)
Mn(21)	10982(1)	3276(1)	−7322(3)	3.5(1)	2.7(1)	1.6(1)	−1.76(9)	0.03(9)	0.18(9)
Mn(22)	11151(1)	1029(1)	−4794(3)	2.18(9)	2.21(9)	2.6(1)	−0.99(8)	0.40(8)	−0.14(9)

Atom	x	y	z	B_j (Å^2)	Atom	x	y	z	B_j (Å^2)
O(11)	5368(5)	3368(6)	−698(16)	4.2(2)	O(12)	4533(5)	3223(5)	5238(13)	2.8(2)
O(13)	5596(5)	5005(6)	3338(14)	2.9(2)	O(14)	8986(5)	3456(6)	−2199(15)	3.7(2)
O(15)	9074(5)	1901(6)	2940(14)	3.3(2)	O(16)	8178(5)	1474(6)	−2017(14)	3.4(2)
O(17)	7619(4)	3993(5)	2020(13)	2.1(2)	O(18)	7026(4)	3635(5)	−1128(13)	2.3(2)
O(19)	6253(6)	4714(7)	−2635(17)	5.4(3)	O(110)	6003(5)	7963(6)	1118(15)	3.6(2)
O(111)	5663(5)	7579(6)	−1457(15)	3.3(2)	O(112)	7532(6)	5785(8)	5534(18)	5.8(3)
O(113)	8311(8)	4688(9)	4159(22)	8.8(4)	N(11)	7124(5)	2622(6)	2506(15)	1.7(2)
N(12)	6706(6)	4439(7)	−1319(18)	3.3(3)	N(13)	5995(6)	7404(7)	64(18)	2.8(2)
N(14)	7665(7)	5254(9)	4372(20)	4.3(3)	C(11)	5617(8)	3270(9)	859(24)	3.4(3)
C(12)	5089(7)	3209(8)	4420(20)	2.4(3)	C(13)	5736(6)	4283(8)	3272(20)	2.0(2)
C(14)	8536(7)	3264(8)	−1165(21)	2.7(3)	C(15)	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C(110)	6435(6)	6518(8)	505(20)	2.0(2)	C(111)	6859(6)	6311(8)	2178(20)	2.0(2)
C(112)	7246(6)	5455(8)	2554(19)	1.9(2)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

C(12)	5089(7)	3209(8)	4420(20)	2.4(3)	C(13)	5736(6)	4283(8)	3272(20)	2.0(2)
C(14)	8536(7)	3284(8)	−1165(21)	2.7(3)	C(15)	[illegible]	[illegible]	[illegible]	[illegible]
C(110)	6435(6)	6518(8)	505(20)	2.0(2)	C(111)	6859(6)	6311(8)	2178(20)	2.0(2)
C(112)	7246(6)	5455(8)	2554(19)	1.9(2)	C(113)	6985(7)	2850(8)	4465(21)	2.7(3)
C(114)	6587(7)	2382(8)	5540(21)	2.7(3)	C(115)	6504(7)	1831(8)	4186(21)	2.7(3)
C(116)	6840(6)	1990(8)	2351(19)	2.0(2)	O(21)	10874(6)	4926(7)	−9322(18)	5.5(3)
O(22)	12599(5)	2677(6)	−8076(15)	4.0(2)	O(23)	10994(7)	3955(8)	−3504(20)	6.7(3)
O(24)	11676(5)	−570(7)	−2331(16)	4.3(2)	O(25)	10429(5)	168(6)	−7031(16)	4.1(2)
O(26)	9853(5)	1509(6)	−1834(15)	3.8(2)	O(27)	12062(4)	704(5)	−6668(13)	2.4(2)
O(28)	11662(4)	1666(5)	−3351(13)	2.3(2)	O(29)	12462(5)	2126(6)	−2490(14)	3.4(2)
O(210)	14996(5)	1188(6)	−5029(14)	2.8(2)	O(211)	15360(5)	453(6)	−7635(14)	3.0(2)
O(212)	13482(6)	−935(7)	−9167(16)	4.7(2)	O(213)	12766(5)	220(6)	−10573(16)	4.3(2)
N(21)	10748(5)	2138(6)	−6636(16)	2.0(2)	N(22)	12311(6)	1670(7)	−3533(16)	2.4(2)
N(23)	14880(5)	818(6)	−6378(16)	2.1(2)	N(24)	1317(6)	−166(7)	−9314(18)	2.7(2)
C(21)	10919(8)	4257(10)	−8489(25)	4.3(4)	C(22)	11952(8)	2934(9)	−7788(22)	3.3(3)
C(23)	10993(9)	3680(11)	−5024(28)	4.9(4)	C(24)	11498(7)	44(9)	−3290(23)	3.4(3)
C(25)	10711(7)	503(9)	−6140(22)	3.0(3)	C(26)	10357(7)	1338(8)	−2980(21)	2.8(3)
C(27)	12687(7)	758(8)	−6478(20)	2.1(3)	C(28)	12870(6)	1191(7)	−4967(19)	1.8(2)
C(29)	13584(6)	1225(8)	−4967(19)	2.1(3)	C(210)	14123(6)	806(8)	−6408(19)	1.9(2)
C(211)	14017(6)	331(8)	−7843(20)	2.2(3)	C(212)	13305(6)	339(8)	−7837(20)	2.1(3)
C(213)	10943(7)	2185(9)	−8633(22)	3.0(3)	C(214)	10437(8)	2915(9)	−9475(23)	3.5(3)
C(215)	9905(8)	3337(9)	−7988(23)	3.4(3)	C(216)	10105(7)	2839(8)	−6276(21)	2.4(3)

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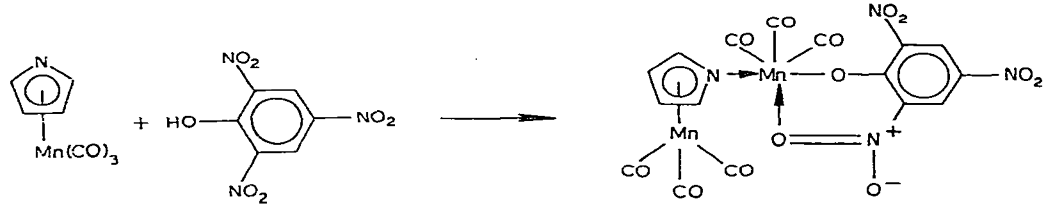
[a] The anisotropic temperature factor is in the form $T = \exp[-1/4(B_{11}h^2a^{*2} + ... + 2B_{23}klb^*c^*)]$.

of the expected PTM picrate $\{[(C_4H_4N)Mn(CO)_3]H\}^+[OC_6H_2(NO_2)_3]^-$.



(I)

The binuclear complex I forms dark purple needle-like crystals, insoluble in hexane and ethanol, poorly soluble in benzene, ether, and CCl_4, and somewhat more soluble in CH_2Cl_2 and acetone.

Crystals of I are triclinic with the following lattice parameters at —120°C: a 19.377(5), b 16.723(6), c 6.800(3) Å, α 85.29(3), β 83.66(3), γ 68.57(3)°, V 2036(2) Å^3, $M = 572.14$ ($C_{16}H_6N_4O_{13}Mn_2$) $d_{calc.}$ 1.86 g/cm^3, $Z = 4$, space group $P\bar{1}$ (two independent molecules). Table 1 lists the atomic coordinates and parameters of the temperature factors; Tables 2 and 3 * contain the bond lengths and angles.

In the binuclear complex I (Fig. 1) a molecule of PTM, is N-coordinated with the second manganese atom via the unshared electron pair of the nitrogen atom of the pyrrolyl ligand, and acts as a two-electron ligand, as in the following complexes previously studied by us: $(OC)_3Mn(\eta^5\text{-}C_4H_4N)Mn(C_4H_3NCOCH_3)(CO)_3$ (II) [2], $(OC)_3Mn(\eta^5\text{-}C_4H_4N)Re(\eta^5\text{-}C_5H_5)(CO)_2$ (III) [3], $[(OC)_3Mn(\eta^5\text{-}C_4H_4N)]_2Mn(CO)_3I$ (IV) [4], and $(OC)_3Mn(\eta^5\text{-}C_4H_4N)Mn(CO)_3(\eta^5\text{-}C_4H_4N)Mn(CO)_2COC_4H_9$ (V) [5]. Additional coordination of the Mn(2) atom with three CO ligands and the formation of a 6-membered chelate metallocycle, involving an oxy-oxygen atom O(7) and one of oxygens O(8) of the *o*-nitrogroup of the picrate anion complete its *fac*-octahedral coordination sphere. Thus, both manganese atoms in the neutral molecule I have an 18-electron shell. A similar completion of an 18-electron shell of a magnanese atom by chelate formation and N-coordination with a nitrogen atom in a pyrrolyl ligand of PTM has been established by us in the acetylation product of PTM [2]. Although the metallocycle in the complex II is 5-membered, chelating ligands in both cases are 3-electron donors, and so in their general stereochemistry complexes I and II are similar to each other.

The pyrrolyl ligand in I is planar and symmetrically bonded to the Mn(1) atom as is evident from the small difference between Mn—C (av. 2.13(1) Å), Mn—N (av. 2.11(1) Å) distances. The bond length distribution in the ligand itself indicates complete delocalization of the π-electron density.

As has already been noted, the coordination of the Mn(2) atom is distorted octahedral. The six-membered metallocycle is non-planar and folded along the O(7)...O(8) line by 17.3 and 10.2° in the two independent molecules, respectively. The nitro-group, N(2)O(8)O(9) participating in coordination with the Mn(2) atom is coplanar to the benzene ring, which plane also contains the oxy-oxygen atom O(7). Two other nitro groups, N(3)O(10)O(11) and

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* In the atom numbering the first figure denotes the number of the molecule (1 or 2) and is not given in the text when denoting atoms.

TABLE 2

BOND LENGTHS, *d* (Å)

Bond	*d*	Bond	*d*	Bond	*d*
Mn(11)—N(11)	2.10(1)	N(11)—C(116)	1.37(2)	O(21)—C(21)	1.19(2)
Mn(11)—C(11)	1.75(2)	N(12)—C(18)	1.41(2)	O(22)—C(22)	1.17(2)
Mn(11)—C(12)	1.79(1)	N(13)—C(110)	1.44(2)	O(23)—C(23)	1.17(2)
Mn(11)—C(13)	1.80(1)	N(14)—C(112)	1.50(2)	O(24)—C(24)	1.13(2)
Mn(11)—C(113)	2.12(1)	C(17)—C(18)	1.45(2)	O(25)—C(25)	1.15(2)
Mn(11)—C(114)	2.15(1)	C(17)—C(112)	1.43(2)	O(26)—C(26)	1.14(2)
Mn(11)—C(115)	2.15(1)	C(18)—C(19)	1.40(2)	O(27)—C(27)	1.27(2)
Mn(11)—C(116)	2.11(1)	C(19)—C(110)	1.37(2)	O(28)—N(22)	1.25(1)
Mn(12)—O(17)	1.989(8)	C(110)—C(111)	1.42(2)	O(29)—N(22)	1.21(1)
Mn(12)—O(18)	2.020(9)	C(111)—C(112)	1.37(2)	O(210)—N(23)	1.23(1)
Mn(12)—N(11)	2.09(1)	C(113)—C(114)	1.40(2)	O(211)—N(23)	1.21(1)
Mn(12)—C(14)	1.79(1)	C(114)—C(115)	1.42(2)	O(212)—N(24)	1.20(2)
Mn(12)—C(15)	1.77(1)	C(115)—C(116)	1.39(2)	O(213)—N(24)	1.21(2)
Mn(12)—C(16)	1.79(1)	Mn(21)—N(21)	2.12(1)	N(21)—C(213)	1.37(2)
O(11)—C(11)	1.19(2)	Mn(21)—C(21)	1.73(2)	N(21)—C(216)	1.38(2)
O(12)—C(12)	1.15(2)	Mn(21)—C(22)	1.75(2)	N(22)—C(28)	1.42(2)
O(13)—C(13)	1.14(1)	Mn(21)—C(23)	1.76(2)	N(23)—C(210)	1.48(2)
O(14)—C(14)	1.18(2)	Mn(21)—C(213)	2.12(1)	N(24)—C(212)	1.47(2)
O(15)—C(15)	1.17(2)	Mn(21)—C(214)	2.14(2)	C(27)—C(28)	1.45(2)
O(16)—C(16)	1.16(2)	Mn(21)—C(215)	2.15(2)	C(27)—C(212)	1.42(2)
O(17)—C(17)	1.23(1)	Mn(21)—C(216)	2,12(1)	C(28)—C(29)	1.41(2)
O(18)—N(12)	1.26(1)	Mn(22)—O(27)	1.988(9)	C(29)—C(210)	1.38(2)
O(19)—N(12)	1.26(2)	Mn(22)—O(28)	2.057(9)	C(210)—C(211)	1.39(2)
O(110)—N(13)	1.23(2)	Mn(22)—N(21)	2.10(1)	C(211)—C(212)	1.37(2)
O(111)—N(13)	1.24(2)	Mn(22)—C(24)	1.81(1)	C(213)—C(214)	1.38(2)
O(112)—N(14)	1.18(2)	Mn(22)—C(25)	1.79(1)	C(214)—C(215)	1.39(2)
O(113)—N(14)	1.26(2)	Mn(22)—C(26)	1.81(1)	C(215)—C(216)	1.38(2)
N(11)—C(113)	1.39(2)				

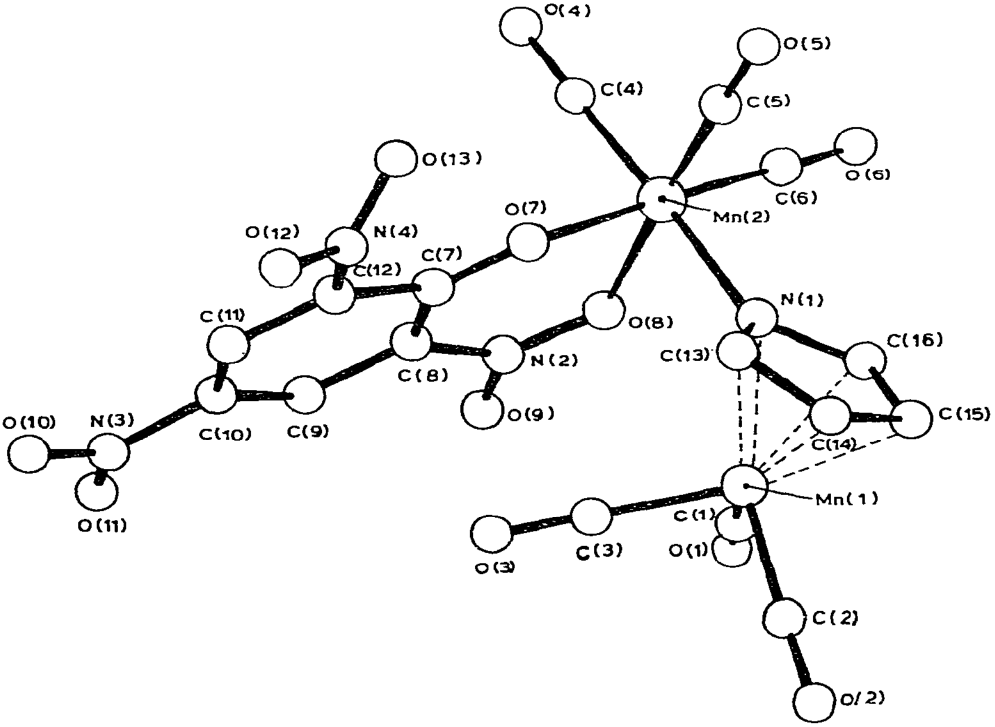


Fig. 1. The structure of complex I.

TABLE 3

BOND ANGLES, ω (°)

Angle	ω	Angle	ω	Angle	ω
C(11)Mn(11)C(12)	91.4(7)	O(17)C(17)C(18)	128(1)	Mn(22)O(28)N(22)	132.3(8)
C(11)Mn(11)C(13)	91.4(7)	O(17)C(17)C(112)	121(1)	Mn(22)N(21)C(213)	124.6(9)
C(12)Mn(11)C(13)	91.6(6)	C(18)C(17)C(112)	110(1)	Mn(22)N(21)C(216)	126.8(9)
O(17)Mn(12)O(18)	86.2(4)	N(12)C(18)C(17)	119(1)	C(213)N(21)C(126)	106(1)
O(17)Mn(12)N(11)	85.7(4)	N(12)C(18)C(19)	115(1)	O(28)N(22)O(29)	118(1)
O(17)Mn(12)C(14)	91.4(5)	C(17)C(18)C(19)	125(1)	O(28)N(22)C(28)	123(1)
O(17)Mn(12)C(15)	94.1(5)	C(18)C(19)C(110)	118(1)	O(29)N(22)C(28)	119(1)
O(17)Mn(12)C(16)	175.8(5)	N(13)C(110)C(19)	119(1)	O(210)N(23)O(211)	123(1)
O(18)Mn(12)N(11)	88.2(4)	N(13)C(110)C(111)	118(1)	O(210)N(23)C(210)	118(1)
O(18)Mn(12)C(14)	92.5(5)	C(19)C(110)C(111)	123(1)	O(211)N(23)C(210)	119(1)
O(18)Mn(12)C(15)	178.1(5)	C(110)C(111)C(112)	116(1)	O(212)N(24)O(213)	126(1)
O(18)Mn(12)C(16)	89.6(5)	N(14)C(112)C(17)	117(1)	O(212)N(24)C(212)	117(1)
N(11)Mn(12)C(14)	176.9(5)	N(14)C(112)C(111)	115(1)	O(213)N(24)C(212)	118(1)
N(11)Mn(12)C(15)	89.9(5)	C(17)C(112)C(111)	128(1)	Mn(21)C(21)O(21)	179(1)
N(11)Mn(12)C(16)	94.1(5)	N(11)C(113)C(114)	110(1)	Mn(21)C(22)O(22)	178(1)
C(14)Mn(12)C(15)	89.4(6)	C(113)C(114)C(115)	106(1)	Mn(21)C(23)O(23)	179(2)
C(14)Mn(12)C(16)	89.0(6)	C(114)C(115)C(116)	108(1)	Mn(22)C(24)O(24)	176(1)
C(15)Mn(12)C(16)	90.1(6)	N(11)C(116)C(115)	109(1)	Mn(22)C(25)O(25)	179(1)
Mn(12)O(17)C(17)	127.3(8)	C(21)Mn(21)C(22)	88.6(7)	Mn(22)C(26)O(26)	178(1)
Mn(12)O(18)N(12)	129.4(8)	C(21)Mn(21)C(23)	90.1(8)	O(27)C(27)C(28)	128(1)
Mn(12)N(11)C(113)	123.5(8)	C(22)Mn(21)C(23)	92.8(8)	O(27)C(27)C(212)	119(1)
Mn(12)N(11)C(116)	127.1(8)	O(27)Mn(22)O(28)	85.7(3)	C(28)C(27)C(212)	113(1)
C(113)N(11)C(116)	107(1)	O(27)Mn(22)N(21)	86.1(4)	N(22)C(28)C(27)	121(1)
O(18)N(12)O(19)	117(1)	O(27)Mn(22)C(24)	93.0(5)	N(22)C(28)C(29)	117(1)
O(18)N(12)C(18)	125(1)	O(27)Mn(22)C(25)	93.0(5)	C(27)C(28)C(29)	122(1)
O(19)N(12)C(18)	118(1)	O(27)Mn(22)C(26)	176.4(5)	C(28)C(29)C(210)	118(1)
O(110)N(13)O(111)	122(1)	O(28)Mn(22)N(21)	87.9(4)	N(23)C(210)C(29)	119(1)
O(110)N(13)C(110)	119(1)	O(28)Mn(22)C(24)	94.3(5)	N(23)C(210)C(211)	117(1)
O(111)N(13)C(110)	118(1)	O(28)Mn(22)C(25)	177.6(5)	C(29)C(210)C(211)	124(1)
O(112)N(14)O(113)	120(1)	O(28)Mn(22)C(26)	90.9(5)	C(210)C(211)C(212)	115(1)
O(112)N(14)C(112)	119(1)	N(21)Mn(22)C(24)	177.5(6)	N(24)C(212)C(27)	116(1)
O(113)N(14)C(112)	115(1)	N(21)Mn(22)C(25)	90.0(6)	N(24)C(212)C(211)	117(1)
Mn(11)C(11)O(11)	179(1)	N(21)Mn(22)C(26)	95.1(5)	C(27)C(212)C(211)	127(1)
Mn(11)C(12)O(12)	178(1)	C(24)Mn(22)C(25)	87.8(7)	N(21)C(213)C(214)	109(1)
Mn(11)C(13)O(13)	179(1)	C(24)Mn(22)C(26)	86.1(7)	C(213)C(214)C(215)	108(1)
Mn(12)C(14)O(14)	177(1)	C(25)Mn(22)C(26)	90.5(7)	C(214)C(215)C(216)	105(1)
Mn(12)C(15)O(15)	177(1)	Mn(22)O(27)C(27)	128.8(8)	N(21)C(216)C(215)	111(1)
Mn(12)C(16)O(16)	178(1)				

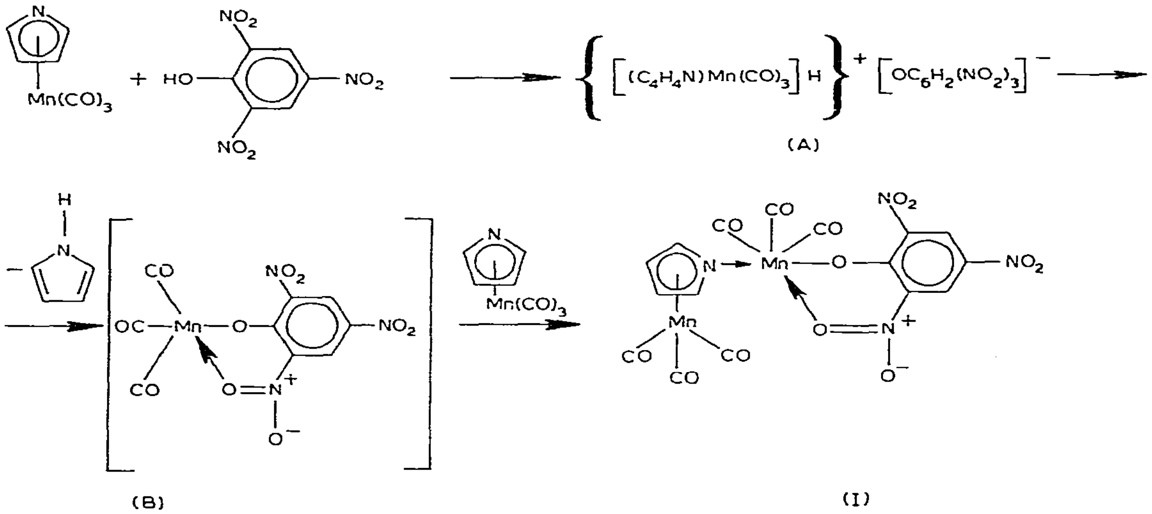
N(4)O(12)O(13), form angles of 6.8 and 8.2°, respectively, with the benzene ring plane. The planar fragment O(7)C(7)C(8)N(2)O(8) of the metallocycle forms a dihedral angle of 68.4° (average) with the pyrrolyl ligand plane, close to the similar angle in complex II (67.0°). In contrast to complex II, where the 5-membered metallocycle is ideally planar, the chelate cycle in I is non-planar, due to a higher conformational flexibility of 6-membered metallocycles.

The lengths of the Mn(2)—N(1) bond (av. 2.10(1) Å) is almost the same as that found in the structures of II (2.104 Å) and IV (2.115 and 2.118 Å). This bond in I, as in the molecules of II and IV, is non-coplanar with the pyrrolyl ligand plane, forming with it an angle of 12.1° (average value).

Other geometrical parameters of I are unexceptional. The lengths of the σ bond Mn(2)—O(7) (av. 1.989(9) Å) and of the donor-acceptor bond Mn(2)—O(8) (av. 2.039(19) Å) are significantly different.

Data of elemental analysis, IR and ^{13}C NMR spectra are in a full agreement with the X-ray crystallographic structure of the complex I. The IR spectrum of I (in CH_2Cl_2) in the region of carbonyl vibrations has five absorption bands at 1950(sh), 1965s, 1975(sh), 2044s, and 2059s cm^{-1}. By analogy with the complex II [2], we assign the ^{13}C NMR signals of I (in CH_2Cl_2) at δ 109.19 and 87.13 ppm to the α and β carbon atoms of the n-coordinated PTM molecule, respectively, and the multiplet signal at δ 220.29 ppm to the carbons of the six carbonyl groups. The signals at δ 165.49, 158.62, 149.66, and 127.10 ppm are assigned to picrate anion carbons.

Considering the possible routes of formation of the binuclear complex I, it can be assumed that this process comprises several stages, protonation of PTM molecule being the first one (the site of proton addition is as yet unknown *).



If we assume that the unstable protonated complex A decomposes further with formation of pyrrole ** and the 16-electron intermediate B, stabilization of the latter via coordination with a molecule of initial PTM will yield the binuclear complex I. This route for the formation of the complex I is similar to that previously proposed by us for the formation of the trinuclear complex V, which is a product of the metallation of PTM with n-butyllithium [5].

Thus, the interaction of PTM with picric acid represents one more example of the ready splitting of the π-bond between a pyrrolyl ligand and a manganese atom and is a specific feature of this π-heterocyclic complex. This splitting results in the formation of coordinatively unsaturated manganese carbonyl fragments, which are capable of interacting with the initial PTM yielding polynuclear complexes with a completed 18-electron shell on the central manganese atom [2,4,5,7].

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* In one of the first papers on azaferrocene it was noted that, on interaction with picric acid, this complex was protonated at the nitrogen atom of the π-pyrrolyl ligand [6], but neither the synthesis nor the characteristics of the isolated crystalline picrate were described.

** Evidently under the reaction conditions used, pyrrole is polymerized and so cannot be identified.

Experimental

PTM was prepared according to the method given in ref. 8. A mixture of 0.1 g (0.49 mmol) PTM and 0.11 g (0.48 mmol) of picric acid in 15 ml CH_2Cl_2 was kept at room temperature for three days. The solvent was removed under argon, and the solid residue washed several times with water (to separate unreacted picric acid) and then with hexane (to separate unreacted PTM), dried in vacuo, and recrystallized from CH_2Cl_2. Dark purple crystals with a decomposition temperature about 150°C were obtained (0.75 g or 54% as calculated for 2 PTM molecules). Elemental analysis. Found: C, 33.60; H, 1.09; N, 10.06; Mn, 18.70. $C_{16}H_6N_4O_{13}Mn_2$ calculated: C, 33.57; H, 1.05; N, 9.79; Mn, 19.23%.

Lattice parameters of crystals of I and intensities of 3309 reflections with $I \geqslant 2\sigma$ were measured at −120°C with an automated 4-circle Syntex $P2_1$ diffractometer (λCu-K_α, graphite monochromator, $\theta/2\theta$ scan, $2\theta \leqslant 42°$); absorptions were not taken into account. The structure was solved by the direct method using the MULTAN program and refined by the least-squares method in a full-matrix isotropic (anisotropic for manganese atoms) approximation. No attempts were made to localize H atoms. Finally, $R = 0.086$, $R_G = 0.088$.

The IR spectrum was obtained with an UR-20 spectrophotometer and the ^{13}C NMR spectrum with a Bruker HX-90 spectrometer (22.63 MHz).

References

1 V.N. Setkina, N.I. Pyshnograeva, P.V. Petrovskii, N.E. Kolobova and D.N. Kursanov, Dokl. Akad. Nauk, 220 (1975) 123.

2 N.I. Pyshnograeva, V.N. Setkina, V.G. Andrianov, Yu.T. Struchkov and D.N. Kursanov, J. Organometal. Chem., 128 (1977) 381.

3 N.I. Pyshnograeva, V.N. Setkina, V.G. Andrianov, Yu.T. Struchkov and D.N. Kursanov, J. Organometal. Chem., 157 (1978) 431.

4 N.I. Pyshnograeva, V.N. Setkina, V.G. Andrianov, Yu.T. Struchkov and D.N. Kursanov, J. Organometal. Chem., 186 (1980) 331.

5 N.I. Pyshnograeva, V.N. Setkina, V.G. Andrianov, Yu.T. Struchkov, and D.N. Kursanov, J. Organometal. Chem., 206 (1981) 169.

6 K.K. Joshi, P.L. Pauson, A.R. Qazi and W.H. Stubbs, J. Organometal. Chem., 1 (1964) 471.

7 W.A. Herrmann, I. Schweizer, P.S. Skell, M.L. Ziegler, K. Wiedenhammer and B. Nuber, Chem. Ber., 112 (1979) 2423.

8 N.V. Kislyakova, N.I. Pyshnograeva, V.F. Sizoy, N.E. Kolobova, V.N. Setkina and D.N. Kursanov, Dokl. Akad. Nauk, 212 (1973) 367.