Table 3. *Comparison of Au—P and Au—X distances in some bisphosphinegold(I) complexes*

Complex*	Au—P (Å)	Au—X (Å)	Reference
$Au(PPh_3)_2Cl\cdot\frac{1}{2}C_6H_6$	2.334 (4), 2.323 (4)	2.500 (4)	Baenziger, Dittemore & Doyle (1974)
$Au(PPh_3)_2Cl$	2.336 (4), 2.317 (4)	2.533 (4)	Bowmaker, Dyason, Healy, Engelhardt, Pakawatchai & White (1987)
$Au(PPh_3)_2SCN$	2.349 (4), 2.346 (4)	2.468 (5)	Muir, Muir & Arias (1982)
$Au(PPh_3)_2NO_3$	2.314 (2), 2.309 (2)	–	Staples, King, Khan, Winpenny & Fackler (1993)
$Au(PPh_3)_2PF_6$	2.312 (4)	–	Staples, King, Khan, Winpenny & Fackler (1993)
$Au(PCy_2Ph)_2Cl$	2.324 (1), 2.300 (1)	2.744 (2)	Muir, Cuadrado, Muir & Barnes (1988)
$Au(CEP)_2Cl$	2.314 (2)	–	Khan, King, Fackler & Winpenny (1993)
$Au(CEP)_2(S_2COEt)$	2.306 (1), 2.310 (2)	2.745 (2) 2.934 (2)	Assefa, Staples & Fackler (1994)
$Au(PPh_3)_2(S_2COEt)$	2.349 (1), 2.315 (2)	2.530 (2) 3.112 (2)	Assefa, Staples & Fackler (1994)
$Au(PBu_3)_2BPh_4$	2.310 (3), 2.305 (4)	–	Staples, Fackler, Khan & Winpenny (1994)
$Au(PCy_3)_2SCN$	2.29 (1), 2.32 (1)	–	Muir, Muir & Lorca (1980)
$[Au(PEt_3)_2][Au(MNT)_2]$	2.315 (3), 2.311 (3)	–	Davila, Staples & Fackler (1994)
$Au(PCy_3)_2Cl$	2.321 (2)	–	Muir, Muir, Pulgar, Jones & Sheldrick (1985)
$Au(PCy_3)_2PF_6$	2.325 (6), 2.324 (6)	–	Cooper, Dennis, Henrick & McPartlin (1980)
$Au(TPA)_2Cl$	2.261 (5)	3.224 (4)	This work

* Cy = cyclohexyl; Ph = phenyl; Et = ethyl; Bu = *n*-butyl; CEP = cyanoethylphosphine; TPA = triazaphosphadamantane; MNT = maleonitriledithiolate $[S(CN)C{=}C(CN)S]^{2-}$.

The crystal quality was below normal as seen from the profiles of several reflections. The data for some reflections were removed because of their asymmetric profiles. The poorer data set required that only the Au, P and Cl atoms could be successfully modelled anisotropically. The structure was solved by direct methods [*SHELXS*86 (Sheldrick, 1985); *SHELXTL-Plus* (Sheldrick, 1990)]. Full-matrix least-squares anisotropic refinement for Au, Cl and P, and isotropic refinement for all remaining non-H atoms was performed (*SHELXS*86 and *SHELXTL-Plus*). H atoms were placed in idealized positions with isotropic displacement parameters fixed at 0.08 $Å^2$.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1043). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Assefa, Z., Staples, R. J. & Fackler, J. P. Jr (1994). *Inorg. Chem.* **33**, 2790–2798.

Baenziger, N. C., Dittemore, K. M. & Doyle, J. R. (1974). *Inorg. Chem.* **13**, 805–811.

Bowmaker, G. A., Dyason, J. C., Healy, P. C., Engelhardt, L. M., Pakawatchai, C. & White, A. H. (1987). *J. Chem. Soc. Dalton Trans.* pp. 1089–1097.

Cooper, M. K., Dennis, G. R., Henrick, K. & McPartlin, M. (1980). *Inorg. Chim. Acta*, **45**, L151–L152.

Darensbourg, M. Y. & Daigle, D. (1975). *Inorg. Chem.* **14**, 1217–1222.

Davila, R. M., Staples, R. J. & Fackler, J. P. Jr (1994). *Acta Cryst.* C**50**, 1898–1899.

Guggenberger, L. J. (1974). *J. Organomet. Chem.* **81**, 271–280.

Khan, Md. N. I., King, C., Fackler, J. P. Jr & Winpenny, R. E. P. (1993). *Inorg. Chem.* **32**, 2502–2505.

Muir, M. M., Cuadrado, S. I., Muir, J. A. & Barnes, C. L. (1988). *Acta Cryst.* B**44**, 1659–1660.

Muir, J. A., Muir, M. M. & Arias, S. (1982). *Acta Cryst.* B**38**, 1318–1320.

Muir, J. A., Muir, M. M. & Lorca, E. (1980). *Acta Cryst.* B**36**, 931–933.

Muir, J. A., Muir, M. M., Pulgar, L. B., Jones, P. G. & Sheldrick, G. M. (1985). *Acta Cryst.* B**41**, 1174–1176.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1990). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.

Staples, R. J., Fackler, J. P. Jr, Khan, M. N. I. & Winpenny, R. E. P. (1994). *Acta Cryst.* C**50**, 191–193.

Staples, R. J., King, C., Khan, M. N. I., Winpenny, R. E. P. & Fackler, J. P. Jr (1993). *Acta Cryst.* C**49**, 472–475.

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cis-Dipyridine Complex of Bis(ω-nitroacetophenonato)manganese(II)

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Abstract

In the title compound, bis(ω-nitroacetophenonato-*O*,*O'*)-bis(pyridine)manganese(II), $[Mn(C_8H_6NO_3)_2(C_5H_5N)_2]$, the ω-nitroacetophenonato (ω-nap) ligands chelate the manganese centre, forming a six-membered ring with a bite angle of 80.13 (11)°. The distance from the metal to the nitro O atom is longer than that from the

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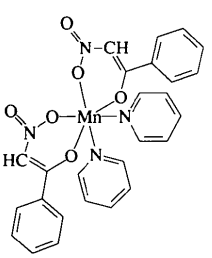
metal to the carbonyl O atom, indicating that the latter is more strongly bound and suggesting a keto-to-enol mechanism preceding the binding of ω-nap to the metal.

Comment

We reported recently the synthesis and structure of the pyridine adduct of bis(ω-nitroacetophenonato)zinc(II) as part of a larger study of complexes of first-row transition elements with polyfunctional ligands (Falvello, Hicke & Mueller, 1995). The ligand ω-nitroacetophenonato (ω-nap) is capable of acting as a hydrogen-bond acceptor, but not a donor, in interactions within a crystalline environment. In the zinc complex, the chelating ω-nap ligand makes a stronger bond to the Zn atom with its carbonyl O atom than with the O atom of the nitro group, thus providing evidence for a mechanism of formation involving a keto–enol tautomerization followed by deprotonation, leaving more negative charge on the carbonyl end of the ligand. We have now synthesized the corresponding manganese complex, (I), the shape of which is expected to yield evidence regarding both this proposed mechanism and a *cis–trans* isomerism between solid state and solution that we have observed in the ethanol adduct (Mueller *et al.*, 1996).



(I)

The complex is isostructural with the zinc compound. It crystallizes in space group *I2/a* with four molecules in the unit cell. The two pyridine (py) ligands are *cis* to each other, and the metal centre is six-coordinate. The molecule lies on a crystallographic twofold axis. The difference between the *M*—O1(carbonyl) and *M*—O3(nitro) distances is less pronounced than that for the zinc complex, but still there is a somewhat shorter metal–ligand distance at the carbonyl end of the chelate: Mn—O1 = 2.118 (3), Mn—O3 = 2.175 (3) Å. In the previously studied complex Zn(ω-nap)$_2$.2py, Zn—O1 = 2.039 (2) and Zn—O3 = 2.152 (2) Å.

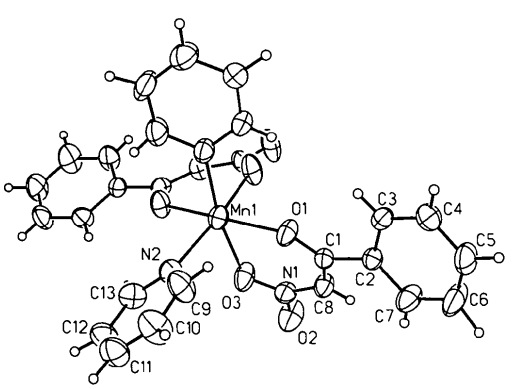


Fig. 1. Structure of the *cis*-dipyridine adduct of bis(ω-nitroacetophenonato)manganese(II). Non-H atoms are represented by their 40% probability ellipsoids. Unlabelled atoms are related to the labelled atoms by a crystallographic twofold axis.

Experimental

To a heated solution of 0.74 g of manganese(II) acetate in 40 ml of 95% ethanol was added 0.5 g of nap in 40 ml of 95% ethanol, affording a red–orange solution. The orange ethanolate precipitated upon cooling. 0.3 g of the ethanolate was dissolved in 15 ml of 95% ethanol. The solution was warmed and 15 ml of pyridine was added, yielding a dark red solution. Evaporation of the solution yielded a mass of dark red crystals.

Crystal data

$[Mn(C_8H_6NO_3)_2(C_5H_5N)_2]$
M_r = 541.42
Monoclinic
I2/a
a = 13.847 (2) Å
b = 12.2000 (10) Å
c = 15.981 (2) Å
β = 105.720 (10)°
V = 2598.9 (5) Å^3
Z = 4
D_x = 1.384 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11.4–15.8°
μ = 0.555 mm^{-1}
T = 298 (2) K
Well formed plate
0.29 × 0.20 × 0.12 mm
Red

Data collection

Nonius CAD-4 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scans (Kopfmann & Huber, 1968)
T_{min} = 0.82, T_{max} = 0.84
2385 measured reflections
2279 independent reflections
1305 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0401
θ_{max} = 24.98°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 14$
$l = -18 \rightarrow 18$
3 standard reflections frequency: 180 min intensity decay: 0.22%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0582
$wR(F^2)$ = 0.1040
S = 1.202
2068 reflections
212 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 1.2622P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = −0.033
$\Delta\rho_{max}$ = 0.270 e Å^{-3}
$\Delta\rho_{min}$ = −0.236 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mn1	1/4	0.03581 (9)	0	0.0454 (3)
O1	0.3674 (2)	0.0211 (3)	0.1162 (2)	0.0541 (9)
O2	0.1833 (3)	−0.2428 (3)	0.1325 (2)	0.0810 (13)
O3	0.1886 (2)	−0.0929 (3)	0.0646 (2)	0.0657 (10)
N1	0.2308 (3)	−0.1594 (3)	0.1232 (2)	0.0485 (10)
N2	0.1610 (3)	0.1598 (3)	0.0495 (2)	0.0477 (10)
C1	0.3853 (3)	−0.0519 (4)	0.1735 (3)	0.0397 (11)
C2	0.4806 (3)	−0.0426 (4)	0.2442 (3)	0.0394 (10)
C3	0.5575 (3)	0.0214 (4)	0.2305 (3)	0.0491 (12)
C4	0.6445 (4)	0.0372 (5)	0.2945 (3)	0.0622 (15)
C5	0.6568 (4)	−0.0090 (5)	0.3745 (4)	0.071 (2)
C6	0.5816 (5)	−0.0725 (5)	0.3898 (4)	0.081 (2)
C7	0.4946 (4)	−0.0892 (5)	0.3253 (3)	0.061 (2)
C8	0.3241 (3)	−0.1419 (4)	0.1769 (3)	0.0478 (12)
C9	0.2051 (4)	0.2286 (5)	0.1125 (4)	0.069 (2)
C10	0.1550 (5)	0.2979 (6)	0.1518 (4)	0.082 (2)
C11	0.0534 (5)	0.3006 (5)	0.1252 (4)	0.070 (2)
C12	0.0035 (4)	0.2317 (5)	0.0595 (4)	0.0618 (15)
C13	0.0612 (4)	0.1640 (5)	0.0245 (3)	0.0559 (14)

Table 2. *Selected geometric parameters (Å, °)*

Mn1—O1	2.118 (3)	O3—N1	1.257 (4)
Mn1—O3^{i}	2.175 (3)	N1—C8	1.361 (5)
Mn1—N2	2.228 (4)	C1—C8	1.397 (6)
O1—C1	1.253 (5)	C1—C2	1.492 (5)
O2—N1	1.242 (4)		
O1—Mn1—O1^{i}	170.3 (2)	C1—O1—Mn1	130.8 (3)
O1—Mn1—O3	80.13 (11)	N1—O3—Mn1	131.1 (3)
O1^{i}—Mn1—O3	92.80 (12)	O2—N1—O3	117.7 (4)
O3^{i}—Mn1—O3	87.6 (2)	O2—N1—C8	119.7 (4)
O1—Mn1—N2	96.52 (13)	O3—N1—C8	122.6 (4)
O3—Mn1—N2	89.80 (13)	O1—C1—C8	125.8 (4)
O1—Mn1—N2^{i}	90.10 (12)	O1—C1—C2	117.3 (4)
O3—Mn1—N2^{i}	169.74 (12)	C8—C1—C2	116.9 (4)
N2—Mn1—N2^{i}	94.4 (2)	N1—C8—C1	125.5 (5)

Symmetry code: (i) $\frac{1}{2} - x, y, -z$.

The crystals decompose slowly upon removal from their mother liquid. The sample was covered with a thin layer of epoxy. There was no significant decay during the course of data collection. The crystals are relatively weak scatterers. Cautious data collection procedures were used. Measured absorption corrections were applied to the data set. Eight complete ψ scans were used, along with three ψ scans of scattering vectors in general directions. The crystal was indexed with a body-centred monoclinic cell, using the shortest repeats in the *ac* plane as the *a* and *c* axes. The use of this 'more reduced' cell, which also has the least obtuse possible β angle for this lattice, is intended to minimize correlation in the refinement of the structure. The symmetry operations used for *I*2/*a* were (x, y, z), $(\frac{1}{2} - x, y, -z)$, $(\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z)$, $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$, $(-x, -y, -z)$, $(\frac{1}{2} + x, -y, z)$, $(\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z)$ and $(x, \frac{1}{2} - y, \frac{1}{2} + z)$. During data collection, variable scan speeds were used, but final scans were forced for all reflections. Thus, the weakest reflections were gathered at the slowest scan speed. The solution and refinement of the structure proceeded routinely. All non-H atoms were located by direct methods. All eleven H atoms were seen in a difference Fourier map, and all were refined freely. Anisotropic displacement parameters were used for all non-H atoms.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4-*PC*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1273). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1993). *CAD-4-PC*. Version 1.2. Enraf–Nonius, Delft, The Netherlands.

Falvello, L. R., Hicke, S. & Mueller, T. E. (1995). *Acta Cryst.* **C51**, 859–861.

Kopfmann, G. & Huber, R. (1968). *Acta Cryst.* **A24**, 348–351.

Mueller, T. E., DiCarlo, E., Zubach, P., Hicke, S., Rabena, M., Falvello, L. R., Migueleiz, E. & Pascual, I. (1996). In preparation.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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$[Cr\{tren(impy)_3\}](ClO_4)_3$, where $tren(impy)_3 = N[CH_2CH_2N{=}C(H)(py)]_3$

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Abstract

The structure of {tris[4-(2-pyridyl)-3-aza-3-butenyl]-amine}chromium triperchlorate, $[Cr\{tren(impy)_3\}](ClO_4)_3$, $[Cr(C_{24}H_{27}N_7)](ClO_4)_3$, where $tren(impy)_3$ is $N[CH_2CH_2N{=}C(H)(py)]_3$, consists of $[Cr\{tren(impy)_3\}]^{3+}$ cations in which the Cr^{III} centre adopts distorted octahedral coordination geometry. The trigonal twist angle of 52° is close to that expected for octahedral Cr^{III} and there is little evidence suggesting coordination of the apical N atom of the tris(2-aminoethyl)-amine backbone of the ligand.

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