X-Ray Molecular Structure of *cyclo*-Bis-(μ-acetato-μ-nitrosyl)-bis[di-μ-acetato-diplatinum(II)]; a Tetranuclear Complex Containing both Nitrosyl and Acetate Bridges

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The crystal structure of the title complex, in the form of an acetic acid solvate $Pt_4(AcO)_6(NO)_2,2AcOH$, has been determined from three-dimensional *X*-ray diffractometer data. Crystals are monoclinic with unit-cell dimensions $a = 23·724(3)$, $b = 8·682(1)$, $c = 14·195(2)$ Å, $\beta = 92·98(1)°$; space group $C2/c$, $Z = 4$. Full-matrix least-squares refinement, by use of 1521 independent reflections, has reached R 0·066.

The complex molecule, which lies around a diad axis, is tetranuclear with the four platinum atoms forming an approximate rectangle of sides 2·944 and 3·311 Å. Each of the two independent metal atoms is bonded to three oxygen atoms from bridging acetate groups and to one nitrogen atom from a bridging nitrosyl group, to give a square-planar co-ordination. The mean Pt–N (1·91 Å) and N–O distances (1·22 Å), and the sp^2 geometry at the bridging nitrogen atom are all consistent with the formulation of the nitrosyl group as NO⁻. The Pt–O distances are unexceptional, mean 2·04 Å. Some Pt · · · Pt distances and the stacking of the molecules suggest that weak metal–metal interactions exist. The solvated acetic acid occurs as isolated hydrogen-bonded pairs of molecules.

STEPHENSON *et al.*[1] reported the preparation of diacetato-platinum(II) and -palladium(II) and suggested that these compounds were trimeric. The palladium complex in particular is a useful catalyst for a number of oxidation reactions involving olefins.[2] An *X*-ray crystal structure determination showed it to be indeed trimeric with a cyclic structure involving bridging acetate groups.[3] Since the platinum complex was reported as not being isomorphous, we set out to determine its crystal structure also. We found that the material studied had a novel tetranuclear structure and contained bridging nitrosyl as well as bridging acetate groups, and had a molecular formula $Pt_4(AcO)_6(NO)_2$. A preliminary account of this work has been published.[4]

Inspection of analysis results and of *X*-ray powder patterns showed that the preparation of diacetato-platinum(II) by the reduction of Pt^{IV} in nitric acid–acetic acid[1,5] may result in one of several nitrogen-containing compounds, although a more recent method[6] of preparing $Pt(AcO)_2$ excludes this possibility.

EXPERIMENTAL

Crystals were obtained as black pleochroic needles containing solvated acetic acid, $Pt_4(AcO)_6(NO)_2,2AcOH$, by recrystallising from chloroform–glacial acetic acid the product obtained using the safer Davidson and Triggs modification[5] of the original preparation.[1] The crystals are elongated along the *c* axis.

Crystal Data.—$C_{16}H_{26}N_2O_{18}Pt_4$, $M = 1314·4$, Monoclinic, $a = 23·724(3)$, $b = 8·682(1)$, $c = 14·195(2)$, $\beta = 92·98(1)°$, $U = 2919·8$ Å³, $D_m = 2·97$, $Z = 4$, $D_c = 2·99$, $F(000) = 2368$. Space group $C2/c$, Cu-K_α radiation, $\lambda = 1·5418$ Å; μ(Cu-K_α) $= 363·9$ cm⁻¹.

Preliminary Weissenberg photographs showed the systematic absences to be: hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, consistent with space groups Cc and $C2/c$; the

latter was shown to be correct from the subsequent solution and refinement of the structure. The crystal used to collect the intensity data was of size *ca.* 0·20 × 0·06 × 0·04 mm and was mounted about its *c* axis on a Siemens off-line four-circle diffractometer. Cu-K_α radiation at a take-off angle of 4·5°, a nickel β filter, and a Na(Tl)I scintillation counter were used. Accurate unit-cell dimensions were obtained by measuring 20 high-angle α_1 reflections. The intensities of 1521 independent reflections were measured (to θ 50°) by the θ—2θ scan technique with a 'five-value' measuring procedure.[7] Of these 185 were judged to be unobserved, having a net count $<2·58\sigma$ (*i.e.* $<99\%$ confidence level). The 040 reflection was measured as a reference every 50 reflections and its net count did not vary noticeably during the course of data collection (*ca.* 4 days). Data were scaled by use of the reference reflection, and Lorentz and polarisation corrections were applied.

Solution and Refinement of the Structure.—The crystal-structure calculations system '*X*-ray '63'[8] and its updated version[9] were used to solve and refine the structure. Calculations were carried out on the Imperial College IBM 7094 and CDC 6400 and the University of London CDC 6600 computers.

A Patterson synthesis showed the positions of the two independent platinum atoms, and isotropic least-squares refinement gave R 0·149. From the resulting difference Fourier all the remaining non-hydrogen atoms were located, and refinement of platinum with anisotropic thermal parameters and isotropic ones for the remaining atoms reduced R to 0·104. (An incorrect solution for the metal atoms gave the low R value of 0·19 but the resulting difference Fourier failed to show the rest of the structure).

At this stage the nitrogen atom of the nitrosyl group was assumed to be a carbon, but this led to an unacceptably low B of 0·1 Å². A chemical analysis was then performed (by the Microanalytical Laboratory, Imperial College) and showed that the compound under study contained nitrogen [Found: C, 13·9; H, 1·8; N, 2·2%. Calc. for $Pt_4(CH_3\text-CO_2)_6(NO)_2,2CH_3CO_2H$: C, 14·6; H, 2·0; N, 2·1%]. When

[1] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.

[2] Netherlands P. 6,510,921, 1966 (*Chem. Abs.*, 1966, **65**, 3753g); Netherlands P. 6,501,827, 1965 (*Chem. Abs.*, 1966, **64**, 4949h); Netherlands P., 6,406,180, 1965 (*Chem. Abs.*, 1966, **64**, 11,091d).

[3] A. C. Skapski and M. L. Smart, *Chem. Comm.*, 1970, 658.

[4] P. de Meester, A. C. Skapski, and J. P. Heffer, *J.C.S. Chem. Comm.*, 1972, 1039.

[5] J. M. Davidson and C. Triggs, *Chem. and Ind.*, 1966, 306.

[6] B.P. 1,214,552, 1970.

[7] A. C. Skapski and P. G. H. Troughton, *Acta Cryst.*, 1970, **B26**, 716.

[8] '*X*-Ray '63' system of programs, J. M. Stewart, University of Maryland Technical Report TR 64 6.

[9] Ref. 8, version of July 1970, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin.

this atom was refined as a nitrogen its temperature factor became satisfactory.

Data were corrected for absorption according to the method of Busing and Levy [10] by use of a 10 × 10 × 10 grid with pathlengths determined by the vector-analysis procedure of Coppens et al.[11] Refinement as previously gave R 0·072. A weighting scheme of the type suggested by Hughes [12] was applied where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geqslant F^*$, with $F^* = 100$ as the final value. Application of the weighting scheme reduced R to 0·067 and gave improved standard deviations. Eleven of the hydrogen atoms could be located on a difference Fourier, and the positions of the other two were calculated. When the hydrogen atoms were included in subsequent refinement as a fixed-atom contribution with isotropic temperature factors of their parent atoms, R reached its final value of 0·066.

When refinement was tried with all non-hydrogen atoms anisotropic only a small improvement in R resulted, but two of the acetate oxygen atoms now had temperature-factors which were ' non-positive definite '. It was decided that the accuracy of the data was probably not sufficient for such a refinement, and since bond lengths and bond angles were virtually identical with those at R 0·066 the refinement was terminated with only platinum anisotropic.

Full-matrix least-squares refinement was used throughout. Atomic scattering factors were taken from ref. 13, except those for hydrogen which were from ref. 14. The real and the imaginary parts of the anomalous dispersion correction for platinum were taken from ref. 15. The

TABLE 1

Fractional co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z
Pt(1)	0·01988(5)	0·06153(13)	0·39687(8)
Pt(2)	0·09635(5)	0·09362(13)	0·24122(8)
O(1)	0·1530(8)	0·012(2)	0·3474(13)
O(2)	0·0884(8)	0·060(2)	0·4514(13)
C(1)	0·1392(12)	−0·050(3)	0·4198(20)
C(2)	0·1851(15)	−0·127(4)	0·4812(25)
O(3)	0·0589(8)	0·266(2)	0·4344(13)
O(4)	0·1029(7)	0·308(2)	0·2985(12)
C(3)	0·0858(10)	0·345(3)	0·3751(18)
C(4)	0·1022(13)	0·506(4)	0·4107(22)
O(5)	0·1009(7)	−0·121(2)	0·1892(13)
O(6)	0·0119(8)	−0·148(2)	0·1341(13)
C(5)	0·0580(12)	−0·197(3)	0·1592(19)
C(6)	0·0671(14)	−0·370(4)	0·1517(23)
N(7)	0·0452(9)	0·172(3)	0·1399(15)
O(7)	0·0583(8)	0·292(2)	0·1015(14)
O(8)	0·2267(12)	0·348(4)	0·400(2)
O(9)	0·2870(13)	0·141(4)	0·415(2)
C(8)	0·2572(20)	0·244(6)	0·366(3)
C(9)	0·2598(22)	0·224(7)	0·263(4)

final fractional co-ordinates of the non-hydrogen atoms and their estimated standard deviations are listed in Table 1, while Table 2 shows the isotropic temperature factors for O, N, and C atoms and the coefficients in the expression

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for the anisotropic temperature factor: $\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$ for the platinum atoms. The co-ordinates of the hydrogen atoms are given in Table 3, and the observed structure amplitudes and the

TABLE 2

Thermal parameters, anisotropic for the platinum atoms and isotropic for all other atoms

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Pt(1)	129(3)	760(19)	341(8)	−58(5)	19(3)	2(8)
Pt(2)	123(3)	717(19)	355(8)	−22(5)	23(3)	−20(8)

Atom	$B/\text{Å}^2$	Atom	$B/\text{Å}^2$
O(1)	3·5(4)	C(1)	3·3(6)
O(2)	3·5(4)	C(2)	5·4(8)
O(3)	3·6(4)	C(3)	2·6(5)
O(4)	3·1(4)	C(4)	4·5(7)
O(5)	2·8(3)	C(5)	3·3(5)
O(6)	3·5(4)	C(6)	4·7(7)
N(7)	2·9(4)	O(7)	3·9(4)
O(8)	7·4(7)	C(8)	8·1(1·1)
O(9)	7·7(7)	C(9)	9·7(1·3)

TABLE 3

Fractional co-ordinates of the hydrogen atoms. Calculated positions in square brackets

Atom	Attached to	x	y	z
H(21)	C(2)	0·193	−0·096	0·547
[H(22)	C(2)	0·176	−0·248	0·482]
[H(23)	C(2)	0·225	−0·110	0·447]
H(41)	C(4)	0·113	0·581	0·365
H(42)	C(4)	0·062	0·569	0·439
H(43)	C(4)	0·143	0·494	0·448
H(61)	C(6)	0·104	−0·402	0·182
H(62)	C(6)	0·064	−0·388	0·083
H(63)	C(6)	0·031	−0·404	0·180
H(91)	C(9)	0·233	0·142	0·214
H(92)	C(9)	0·250	0·334	0·229
H(93)	C(9)	0·302	0·191	0·247
H(8)	O(8)	0·221	0·346	0·476

calculated structure factors are listed in Supplementary Publication No. SUP 20668 (6 pp.).*

DISCUSSION

Description of the Structure.—This X-ray study has proved that the title complex possesses a tetranuclear structure which is shown in Figure 1. The more important interatomic distances and bond angles are quoted in Table 4, while the arrangement in the unit cell of the complex molecules and of the acetic acid of solvation is shown as a stereoscopic pair of drawings [16] in Figure 2.

The complex molecule lies around a diad axis and the four metal atoms form a slightly oblique rectangle of sides 2·944 and 3·311 Å.† The platinum atoms are joined together by double acetate bridges spanning the two shorter sides, while the other two sides are each

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† The rectangle is not strictly planar [see Figure 1(a)] with the platinum atoms ca. ±0·14 Å from the least-squares plane. Since they are not joined together by direct bonds there is, of course, no reason other than the restraints imposed by the bridging groups why the metal atoms should adopt any particular configuration.

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[11] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.
[12] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.
[13] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.
[14] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[15] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.
[16] C. K. Johnson, ORTEP Thermal Ellipsoid Plotting Program, Oak Ridge National Laboratory Report, 1965, ORNL 3794.

bridged by one nitrosyl and one acetate group. Thus each of the two independent platinum atoms is bonded
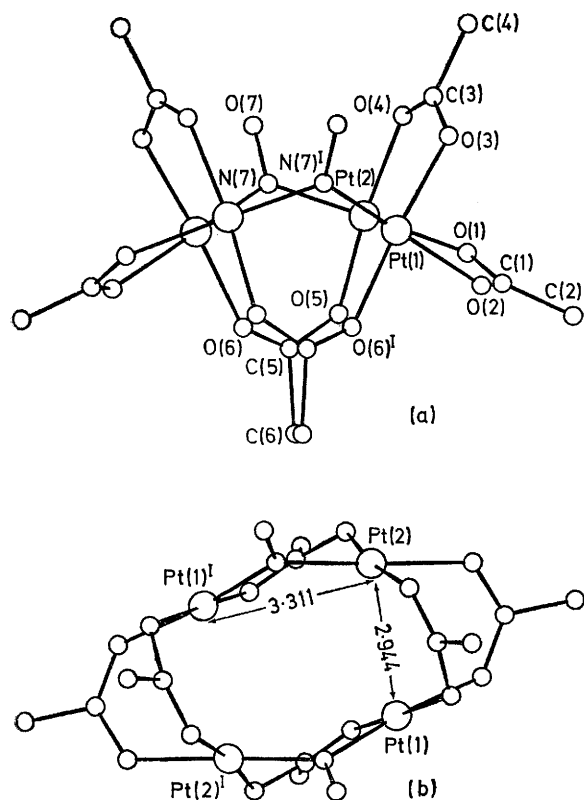

FIGURE 1   Two views of the molecular structure of Pt₄(acetate)₆-(NO)₂; (b) is viewed down a diad axis which passes through the centre of the molecule. The atom labelling system is shown

to one nitrogen and three oxygen atoms to give a square-planar co-ordination. Table 5 shows details of the

TABLE 4

Selected interatomic distances (Å) and bond angles (°) with estimated standard deviations in parentheses

(a) Distances

Pt(1)–O(2)	2·053(19)	Pt(2)–O(1)	2·091(18)
Pt(1)–O(3)	2·062(19)	Pt(2)–O(4)	2·032(18)
Pt(1)–O(6ᴵ)	2·008(19)	Pt(2)–O(5)	2·007(18)
Pt(1)–N(7ᴵ)	1·869(21)	Pt(2)–N(7)	1·955(21)
	Mean Pt–O	2·042	
	Mean Pt–N	1·912	

Pt(1) ··· Pt(2)	2·944(2)	Pt(1) ··· Pt(1ᴵᴵ)	3·300(2)
Pt(1ᴵ) ··· Pt(2)	3·311(2)		

C(1)–O(1)	1·22(3)	C(5)–O(5)	1·27(3)
C(1)–O(2)	1·31(3)	C(5)–O(6)	1·21(3)
C(3)–O(3)	1·28(3)	C(8)–O(8)	1·27(6)
C(3)–O(4)	1·22(3)	C(8)–O(9)	1·31(6)
	Mean C–O	1·26	

C(1)–C(2)	1·51(4)	C(5)–C(6)	1·52(4)
C(3)–C(4)	1·53(4)	C(8)–C(9)	1·49(7)
	Mean C–C	1·51	

N(7)–O(7)	1·22(3)	O(8ᴵᴵᴵ) ··· O(9)	2·67(4)

(b) Angles

O(2)–Pt(1)–O(3)	90·5(7)	O(1)–Pt(2)–O(4)	89·4(7)
O(3)–Pt(1)–N(7)	89·1(8)	O(4)–Pt(2)–N(7)	90·4(8)
N(7ᴵ)–Pt(1)–O(6ᴵ)	96·2(9)	N(7)–Pt(2)–O(5)	95·5(8)
O(6ᴵ)–Pt(1)–O(2)	84·2(8)	O(5)–Pt(2)–O(1)	84·6(7)
O(2)–Pt(1)–N(7ᴵ)	174·0(9)	O(1)–Pt(2)–N(7)	178·3(8)
O(3)–Pt(1)–O(6ᴵ)	174·7(7)	O(4)–Pt(2)–O(5)	172·4(7)
	Pt(1ᴵ)–N(7)–Pt(2)	119·9(1·2)	
	Mean Pt–N–O	120·0(1·7)	
	Mean Pt–O–C	126·1(1·7)	
	Mean O–C–O	128·0(2·5)	
	Mean O–C–C	116·0(2·6)	

Superscripts refer to atoms in the following positions:

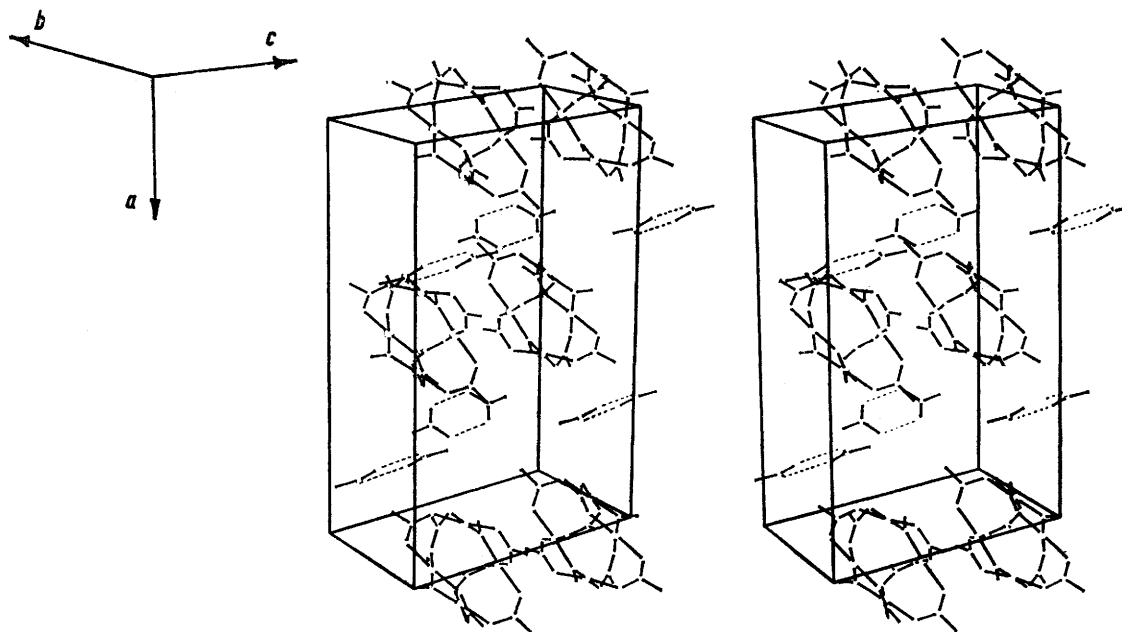I −x, y, ½ − z   III ½ − x, ½ − y, 1 − z
II −x, −y, 1 − z

FIGURE 2   A stereoscopic view showing the packing of the complex molecules and of the hydrogen-bonded pairs of acetic acid

planarity of various groups in the structure. It can be seen that for both Pt(1) and Pt(2) the four co-ordinating atoms have an appreciably greater deviation from planarity than is found for the various acetate groups. This suggests that these distortions from strictly square-planar co-ordination, although slight, are genuine, and

TABLE 5

Planarity of groups of atoms in the structure. The equations of the planes are expressed as $Px + Qy + Rz = S$

P	Q	R	S	Deviation (Å) of atoms from plane
−9·85	−0·49	13·18	5·06	O(2) 0·047, O(3) −0·046, O(6$^{\mathrm{I}}$) −0·048, N(7$^{\mathrm{I}}$) 0·047, Pt(1) * −0·056
19·07	2·04	−8·34	0·07	O(1) −0·027, O(4) 0·027, O(5) 0·027, N(7) −0·026, Pt(2) * −0·057
3·00	7·44	6·98	2·97	O(1) −0·001, O(2) −0·001, C(1) 0·004, C(2) −0·001, Pt(1) * 0·314, Pt(2) * −0·304
19·76	−3·04	5·46	2·72	O(3) 0·008, O(4) 0·009, C(3) −0·022, C(4) 0·006, Pt(1) * −0·346, Pt(2) * 0·218
−8·06	−0·94	13·49	1·86	O(5) −0·003, O(6) −0·004, C(5) 0·009, C(6) −0·003, Pt(1$^{\mathrm{I}}$)* −0·362, Pt(2) * 0·534
12·90	−4·45	−9·83	−1·55	Pt(1$^{\mathrm{I}}$) 0·003, Pt(2) 0·003, N(7) −0·009, O(7) 0·004
18·62	5·38	−0·38	5·95	O(8) −0·005, O(9) −0·005, C(8) 0·013, C(9) −0·005

* Atoms not included in the definition of the plane.

are probably a consequence of the strain required to achieve the cyclic structure.

The difference between the two independent Pt–N distances is probably not significant (mean 1·912 Å). Ibers and his co-workers [17] have shown, on the basis of a number of structure determinations of nitrosyl–metal complexes, that where the M–N bond is very short and the system M–N–O is linear the ligand can be considered as NO$^+$, whereas for NO$^-$ the metal–nitrogen distance is appreciably longer and the angle at the nitrogen is ca. 120° (see Table 7 in ref. 17). This distinction is well illustrated in the three compounds where both types of nitrosyl groups are present together, i.e. in Mn$_2$(π-C$_5$H$_5$)$_2$(NO)$_3$NO$_2$,[18] Cr$_2$(π-C$_5$H$_5$)$_2$(NO)$_3$NH$_2$,[19] and [RuCl-(NO)$_2$(PPh$_3$)$_2$][PF$_6$].[20] In the present compound the mean Pt–N distance and the almost perfect sp^2 geometry at the nitrogen atom are consistent with the formulation of the ligand as NO$^-$.

Originally it was suggested [17] that in NO$^-$ the N–O distance would be longer than in NO$^+$, but more recent studies [21] show that this distance is a poor criterion for distinguishing between NO$^+$ and NO$^-$ largely because of insufficient accuracy in published distances. Thus,

while the observed N–O distance of 1·22(3) Å in our complex is at the long end of the range reported, the standard deviation is high.

Each bridging acetate group lies askew to the line joining the two bridged Pt atoms [this is best seen in Figure 1(b)], so that these atoms are appreciably on either side of the plane defined by the acetate group (Table 5). The six independent Pt–O distances are in the range 2·007—2·091 Å, mean 2·042 Å. While there are many known Pt$^{\mathrm{IV}}$–O distances, it is not easy to find comparable Pt$^{\mathrm{II}}$–O since in the few relevant structures which have been reported varying degrees of trans-influence are observed. However, the distances found in this complex can be regarded as unexceptional if one compares them to a range of 1·98—2·07 Å in Pt$_2$(acac)$_2$-(C$_3$H$_5$)$_2$,[22] and 1·968—2·072 Å in K[Pt(acac)$_2$Cl] [23] (acac = acetylacetonate).

In two recently reported compounds, [Co(NH$_3$)$_5$(NO)]-Cl$_2$ [24] and trans-[Co(en)$_2$Cl(NO)]ClO$_4$ (en = ethylenediamine),[25] the nitrosyl group has been shown to exert a very strong trans-influence. In the present complex the mean Pt–O(trans to NO) is 2·072 Å, and the mean Pt–O(trans to O) is 2·027 Å. The difference of 0·045 Å between these means is on the borderline of significance, and suggests that while a trans-influence may be present it is almost certainly weak. This different behaviour is probably due to the fact that here one has bridging nitrosyl groups, while in the other two complexes a terminal NO$^-$ group is involved.

On the longer side of the rectangle of the four metal atoms, the Pt · · · Pt separation is 3·311 Å and the Pt · · · Pt vector makes angles of ca. 12 and 20° with the planes defining the square-planar co-ordination about Pt(1) and Pt(2) respectively. Furthermore, this vector is within ca. 30° of the Pt–N bonds. Clearly no metal–metal interaction is likely in these circumstances. On the other hand, the shorter side of the rectangle has a Pt(1) · · · Pt(2) distance of 2·944 Å, and this vector makes an angle of ca. 73° with the co-ordination plane about Pt(1). On the other side of Pt(1) lies its centro-symmetrically related neighbour in another molecule at 3·300 Å, and this distance is not spanned by any bridging group. The Pt(1) · · · Pt(1$^{\mathrm{II}}$) vector makes an angle of ca. 74° with the same plane. Thus the geometry about Pt(1) could be visualised as pseudo-octahedral. The vector Pt(1) · · · Pt(2) also makes an angle of ca. 73° with the co-ordination plane about Pt(2), but on the other side of Pt(2) there are no near neighbours. These geometrical relationships are shown schematically in Figure 3.

These Pt · · · Pt separations may be compared with

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[25] D. A. Snyder and D. L. Weaver, Inorg. Chem., 1970, 9, 2760.

the distance found in the metal, 2·78 Å,[26] and also with those found in the three compounds where strong Pt–Pt bonds are known to exist, $i.e.$ 2·647 in $Pt_2S(CO)$-$(PPh_3)_3$,[27] 2·633 in $FePt_2(CO)_5[P(OPh)_3]_3$,[28] and a mean
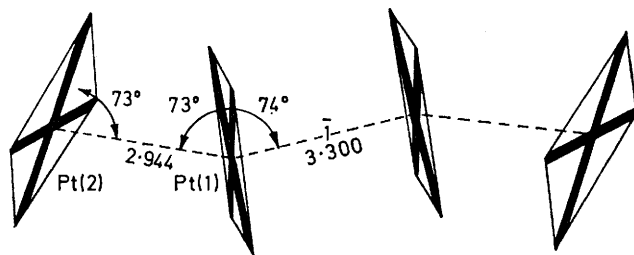

FIGURE 3 A schematic drawing showing the orientation between the co-ordination planes at the Pt atoms and the possible Pt · · · Pt interactions, both within the molecule and between it and its centrosymmetrically related neighbour

of 2·58 Å in $(C_8H_{12})_3Pt_3(SnCl_3)_2$.[29] Thus any metal–metal interactions in the present complex are likely to be weak, but there are many compounds where Pt · · · Pt distances in the range 2·85—3·4 Å are found and where metal–metal interactions are generally accepted to occur.[30] The fact that in this compound such interactions are present is supported by the intense colouration of the crystals and the pleochroism. The crystal optics support the suggestion that the interaction is

approximately along the ' line ' followed by Pt(2) · · · Pt(1) · · · Pt(1^{II}) · ◦ Pt(2^{II}), although it is difficult to say whether it is limited to being within a molecule, or whether it extends between neighbouring molecules as well.

The acetic acid molecules occur in the structure as isolated centrosymmetrically related hydrogen-bonded pairs, with an O–H · · · O separation of 2·67 Å. Although one would expect these solvate molecules to have a somewhat higher thermal motion than the complex, it is possible that the thermal parameters obtained for the four acetic acid atoms to some extent reflect incomplete site occupancy. This conclusion is consistent with the analytical results, but we felt that the accuracy of the data did not justify the computational effort involved in getting a precise measure of the occupancy in this particular crystal.

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