Synthesis of *o*-Nitrophenylplatinum(IV) Complexes; Crystal and Molecular Structure of Dichlorobis(2-nitrophenyl-*C'O*)platinum(IV)

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The reactions between $[Pt\{2\text{-}C_6H_4N(O)O\}_2]$ and halogens or MeI give complexes $[Pt\{2\text{-}C_6H_4N(O)O\}_2X_2]$ [X = Cl (**1**), Br, or I] or $[Pt\{2\text{-}C_6H_4N(O)O\}_2Me(I)]$, respectively. Complex (**1**) reacts with bidentate ligands L–L giving $[Pt(2\text{-}C_6H_4NO_2)_2Cl_2(L\text{–}L)]$ (L–L = 1,10-phenanthroline or 2,2'-bipyridyl). The crystal structure of (**1**) shows octahedral co-ordination with the halogen atoms mutually *trans* and the chelating *o*-nitrophenyl ligands mutually *cis*.

We have described the synthesis of *o*-nitrophenyl complexes of Au^I,[1] Au^{III},[2] Pt^{II},[3] and Rh^{III},[4] using bis(*o*-nitrophenyl)mercury as a transmetallating agent. Some of the molecular structures show interesting differences in the C–C, C–N, and N–O bond distances of the nitrophenyl group that may correspond to differing degrees of electron withdrawal by the nitro group. Thus, in the complex $[Rh\{2\text{-}C_6H_4N(O)O\}_2Cl(CO)]$ [4] the nitro group acts as a strong π acceptor of electron density from the aromatic ring, whereas in the complexes of Pt^{II} [3] and Au^I [1b] such withdrawal is smaller or unobservable. One factor influencing such differences could be the higher oxidation state of the metal in the rhodium complex; we therefore considered it of interest to extend our study to platinum(IV) complexes. Such structural investigations are also of interest in the light of recent controversy [5] about the electron-withdrawing behaviour of the nitro group in aromatic compounds.

Although several methods of preparing *o*-nitrophenyl complexes have been tested,[6] the method that we use [*via* organomercury(II) compounds] is the most general; we have succeeded in preparing complexes with monodentate or (for the first time) [3,4] C,O-chelating *o*-nitrophenyl ligands. Although we have not been able to use the 'organomercury(II) route' to prepare platinum(IV) complexes, we report in this paper the synthesis starting from the corresponding platinum(II) complexes.[3] The synthetic method (halogen or MeI oxidative-addition reactions) is well known, but we are interested in preparing complexes with the *o*-nitrophenyl ligand in both co-ordination modes because we have proposed [3] a method of distinguishing them by i.r. spectroscopy.

Halogen or MeI oxidative-addition reactions to alkylplatinum(II) complexes have been widely studied, but there are comparatively few studies of oxidative additions to aryl complexes in spite of the different behaviour observed in such reactions.[7] In addition, it is surprising that no *X*-ray crystal structure of such platinum(IV) complexes [8] has been established, since there are several isomers that can be obtained. Indeed, few arylplatinum(IV) complexes of any kind have been characterized by *X*-ray diffraction.[9]

Results and Discussion

Synthesis.—The salt $K_2[PtCl_6]$ does not react with $[Hg(2\text{-}C_6H_4NO_2)_2]$ (1:2) even on refluxing in ethanol (4 h). Complexes of the type $[PtRCl_4L]^-$ (R = Ph or $4\text{-}MeC_6H_4$; L = NH_3) have been prepared using the corresponding arylmercurials as transmetallating agents.[10] It is possible that the electron-withdrawing character of the nitro group and/or its *ortho* position in the ring could be responsible for the inertness of $[Hg(2\text{-}C_6H_4NO_2)_2]$ towards the platinum(IV) complex.

Nevertheless *o*-nitrophenylplatinum(IV) complexes can easily be prepared by oxidative-addition reactions starting from $[Pt\{2\text{-}C_6H_4N(O)O\}_2]$. Thus, it reacts with halogens to give $[Pt\{2\text{-}C_6H_4N(O)O\}_2X_2]$ [X = Cl (**1**), Br (**2**), or I (**3**)] and with MeI to give $[Pt\{2\text{-}C_6H_4N(O)O\}_2Me(I)]$ (**4**). Complex (**1**) reacts with 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bipy) giving complexes of the type $[Pt(2\text{-}C_6H_4NO_2)_2Cl_2(L\text{–}L)]$ [L–L = phen (**5**) or bipy (**6**)]. Two types of arylplatinum(II) complexes have been treated with halogens (X_2): (*a*) $[PtR_2L_2]$ [R = Ph, L = PEt_3, X = Cl, Br, or I; R = C_6F_5, L = PEt_3, PBu_3, $AsPh_3$ or L_2 = bipy, phen, $Ph_2As(CH_2)_2AsPh_2$] and (*b*) $[PtR(X)L_2]$ (R = Ph, $2\text{-}FC_6H_4$, or $4\text{-}FC_6H_4$, X = Cl, L = PEt_3; R = C_6F_5, X = Cl or Br, L = PEt_3). The results [7] are difficult to systematize because, depending on the halogen used and on the nature and geometry of the platinum(II) complex, other reactions instead of, or as well as, the addition reaction (*e.g.* displacement of one or both aryl groups) have been observed.

The results of oxidative-addition reactions of MeI to arylplatinum(II) complexes are extremely erratic.[7] Thus, the only complexes studied $[PtR_2L_2]$ give the following: R = Ph, L = PEt_3, mixtures; R = Ph, L_2 = bipy or phen, $[PtPh_2Me(I)(L\text{–}L)]$; R = $2\text{-}MeC_6H_4$, L = PPh_3, pyridine (py), or cycloocta-1,5-diene (cod), $[PtMeI_3(PPh_3)_2]$, $[PtR(Me)I_2(py)_2]$, or $[PtR(I)(cod)]$; R = C_6F_5, L = various N-, P-, and As-donor ligands, no reaction. Therefore $[Pt\{2\text{-}C_6H_4N(O)O\}_2]$ is the only arylplatinum(II) complex whose reactions with Cl_2, Br_2, I_2, and MeI have been studied and for which the products of the oxidative-addition reactions have been isolated.

Structure of the Complexes.—For most oxidative-addition reactions of X–Y to a square-planar platinum(II) complex the initial product has been shown [11] to be the result of co-ordinating X and Y mutually *trans*. However such an isomer is often not the most thermodynamically stable and an isomerization usually occurs. For arylplatinum complexes, the proposed structures of the corresponding platinum(IV) complexes (usually based on n.m.r. data) generally involve a *cis*-configuration of the added ligands.[7]

We have established the structure of complex (**1**) by *X*-ray crystallography. Figure 1 and Table 1 show that (**1**) adopts an octahedral co-ordination with the halogen atoms mutually *trans* and both *o*-nitrophenyl ligands situated approximately in

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* *Supplementary data available:* structure factors, H-atom co-ordinates, thermal parameters can be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany, quoting reference number CSD/52065 and the full literature citation.

Table 1. Bond lengths (Å) and angles (°) for complex (**1**)

Cl(1)–Pt	2.300(2)	Cl(2)–Pt	2.302(2)	C(3)–C(4)	1.399(9)	C(4)–C(5)	1.380(11)
N(1)–O(1)	1.278(7)	N(1)–O(3)	1.200(7)	C(5)–C(6)	1.397(8)	C(6)–N(1)	1.432(10)
N(2)–O(2)	1.270(7)	N(2)–O(4)	1.204(7)	C(7)–Pt	1.997(6)	C(7)–C(8)	1.369(11)
O(1)–Pt	2.173(5)	O(2)–Pt	2.166(5)	C(8)–C(9)	1.402(9)	C(10)–C(9)	1.384(10)
C(1)–Pt	1.995(6)	C(1)–C(2)	1.392(10)	C(10)–C(11)	1.389(12)	C(11)–C(12)	1.406(9)
C(1)–C(6)	1.400(8)	C(2)–C(3)	1.385(9)	C(12)–N(2)	1.427(10)	C(12)–C(7)	1.391(8)
Cl(1)–Pt–Cl(2)	179.4(2)	Cl(1)–Pt–O(1)	92.5(2)	Pt–O(2)–N(2)	112.4(5)	Pt–O(1)–N(1)	111.3(5)
Cl(2)–Pt–O(1)	87.1(2)	Cl(1)–Pt–O(2)	89.6(2)	Pt–C(1)–C(6)	113.1(5)	Pt–C(1)–C(2)	129.6(4)
Cl(2)–Pt–O(2)	90.0(2)	O(1)–Pt–O(2)	95.8(3)	C(1)–C(2)–C(3)	119.4(6)	C(2)–C(1)–C(6)	117.2(6)
Cl(1)–Pt–C(1)	89.0(2)	Cl(2)–Pt–C(1)	91.4(2)	C(3)–C(4)–C(5)	119.9(6)	C(2)–C(3)–C(4)	122.0(8)
O(1)–Pt–C(1)	78.9(3)	O(2)–Pt–C(1)	174.5(3)	N(1)–C(6)–C(1)	116.8(6)	C(4)–C(5)–C(6)	117.2(6)
Cl(1)–Pt–C(7)	91.4(2)	Cl(2)–Pt–C(7)	88.9(2)	C(1)–C(6)–C(5)	124.0(7)	N(1)–C(6)–C(5)	119.0(6)
O(1)–Pt–C(7)	173.8(3)	O(2)–Pt–C(7)	79.4(3)	Pt–C(7)–C(12)	112.7(6)	Pt–C(7)–C(8)	130.0(5)
C(1)–Pt–C(7)	105.9(3)	O(1)–N(1)–O(3)	120.7(7)	C(7)–C(8)–C(9)	121.0(7)	C(8)–C(7)–C(12)	117.2(6)
O(1)–N(1)–C(6)	117.3(5)	O(3)–N(1)–C(6)	121.9(6)	C(9)–C(10)–C(11)	119.3(7)	C(8)–C(9)–C(10)	121.1(8)
O(2)–N(2)–O(4)	120.0(7)	O(2)–N(2)–C(12)	116.9(5)	N(2)–C(12)–C(7)	118.3(6)	C(10)–C(11)–C(12)	118.0(6)
O(4)–N(2)–C(12)	123.1(6)			C(7)–C(12)–C(11)	123.3(7)	N(2)–C(12)–C(11)	118.3(6)

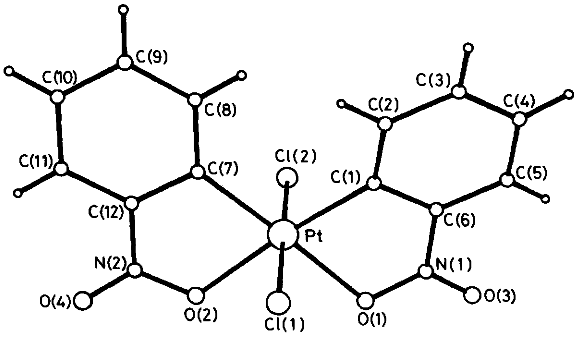


Figure. The molecule of complex (**1**) in the crystal, showing the atom numbering scheme. Radii arbitrary, H atoms omitted

the equatorial plane acting as chelating ligands and mutually *cis*. The angles between the ligand plane and the two aromatic rings are 7° for C(7)—C(12) and 165° for C(1)—C(6).

The average Pt–C [1.996(6) Å] and Pt–Cl [2.301(2) Å] bond lengths are somewhat shorter than in the anionic complex *trans*-$[\mathrm{Pt(C_6H_3Me\text{-}4\text{-}NO_2\text{-}3)(NH_3)Cl_4}]^-$ [Pt–C 2.06(2), Pt–Cl 2.316(6), 2.319(6) Å] [9b] and in the cationic carbenoid complex $[\mathrm{Pt(C_6H_3NHCNHMe\text{-}2\text{-}Cl\text{-}5)(PEt_3)_2Cl_2}]^+$ [Pt–C(Ph) 2.034(11), Pt–Cl 2.415(5) (*trans* to Ph), 2.372(3) Å (*trans* to carbene C)].[9c] It is difficult to rationalize these differences because the compounds are not closely similar.

A comparison of complex (**1**) with the platinum(II) complex $[\mathrm{Pt\{2\text{-}C_6H_4N(O)O\}(2\text{-}C_6H_4NO_2)(PPh_3)}]$ [3] shows that the mutually *trans* $\mathrm{Pt^{II}}$–O [2.138(6) Å] and $\mathrm{Pt^{II}}$–C [1.983(8) Å] are marginally shorter than in the platinum(IV) complex. Our speculation that platinum(IV) might induce a greater electron-withdrawing capacity of the nitro group seems therefore not to have been confirmed, since in such a case a shortening of the $\mathrm{Pt^{IV}}$–O bond distance might be observed. (However, other factors such as a change in metal hybridization will also influence the bond lengths.) This being so, it is not surprising that the dimensions of the nitro group are similar to those of the chelating ligand in the platinum(II) complex.

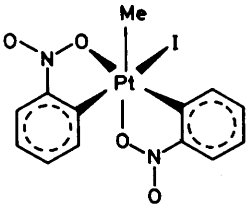
The nitro groups are approximately coplanar with their phenyl rings (dihedral angles 5 and 12°) and are co-ordinated to a metal centre that withdraws electron density from them {judging from the lengthening of the N–O(Pt) [1.270(7) and 1.278(7) Å] and the shortening of the C–N [1.427(10), 1.432(10) Å] bond lengths with respect to the monodentate ligand in the platinum(II) complex, with N–O 1.22—1.23(1) and C–N 1.468(12) Å}. However, instead of displaying groups of long and short C–C bonds, as observed in $[\mathrm{Rh\{2\text{-}C_6H_4N(O)O\}_2Cl(CO)}]$ [1.436(5)—1.508(7) and 1.233(7)—1.298(8) Å],[4] complex (**1**) shows values in the range 1.406(9)—1.369(11) Å, similar to those found in the monodentate nitrophenyl group of the above-mentioned platinum(II) complex [1.355(13)—1.398(12) Å], where the nitro group is rotated by 48° with respect to its phenyl ring.

Complexes (**1**)—(**3**), (**5**), and (**6**) are too insoluble in all solvents to study their n.m.r. spectra. However, the i.r. spectra allow tentative structural assignments. Those of complexes (**1**)—(**3**) are almost identical in the range 4 000—400 cm^{-1} suggesting that the bromo- and iodo-complexes have the same stereochemistry as that of (**1**). Although two i.r.-active ν(X–Pt–X) bands are expected for these three complexes, only one can be assigned by comparing their 400—200 cm^{-1} regions [X = Cl, 360m; Br, 265m (or 275); and I, <200 cm^{-1}]. As complexes (**5**) and (**6**) show a medium-intensity band at 350 and 348 cm^{-1} respectively that can be assigned to the *trans* Cl–Pt–Cl group, we suggest that the nitrogen atoms of the bidentate ligands occupy the same positions as the oxygen atom in (**1**), the nitrophenyl ligands then being monodentate.

We have previously assigned [3] a band at 270—285 cm^{-1} in the *o*-nitrophenylplatinum(II) complexes to a Pt–O vibration, because it appears only in complexes containing chelating *o*-nitrophenyl groups. However, the presence of a medium-intensity band around 270 cm^{-1} in the spectra of all the platinum(IV) complexes gives rise to serious doubts about such an assignment because of its presence in (**5**) and (**6**).

As has been observed with other *o*-nitrophenyl complexes,[1–4] the position of the $\nu_{\mathrm{asym}}(\mathrm{NO_2})$ band in (**1**)—(**6**), which appears in the range 1 530—1 510vs cm^{-1}, is not influenced by the type of co-ordination of the nitrophenyl group but $\nu_{\mathrm{sym}}(\mathrm{NO_2})$ is observed at 1 260—1 270 cm^{-1} when the nitro group is co-ordinated [in complexes (**1**)—(**4**)], or at 1 360vs cm^{-1} when it is not [in (**5**) and (**6**)].

The ^{1}H n.m.r. spectrum of complex (**4**) shows that it is only one of the six possible diastereoisomers (the remaining five could not be distinguished by n.m.r. spectroscopy) because only one peak is observed for the methyl group [δ 1.97 p.p.m., ^2J(PtH) = 78 Hz]. The four phenyl protons appear as four multiplets at around δ 6.2, 7.1, 7.4, and 7.7 p.p.m. That at 7.1 p.p.m. contains 15 peaks; two types of phenyl groups are therefore present in (**4**) and it must be one of the four diastereoisomers containing iodide *cis* to the methyl group.



(4)

Moreover the value of ^2J(PtH) in methylplatinum(IV) complexes is very sensitive to the nature of the *trans* ligand for a given type of complex.[11] The only complexes [7b] similar to (**4**) are [Pt(XC_6H_3)$_2$Me(I)(bipy)] for which ^2J(PtH) = 69.0—72.0 Hz, with iodide *trans* to the methyl group. Therefore, in complex (**4**) the methyl group should be *trans* to a ligand with less *trans* influence than iodide, *i.e.* an oxygen atom. As all reported[7] diarylplatinum(IV) complexes, including (**1**)—(**3**), (**5**), and (**6**), have both aryl groups in *cis* position we suggest for (**4**) the structure shown. The multiplet at 6.2 p.p.m. arises from hydrogen atoms *ortho* to platinum [δ 6.23 and 6.22 p.p.m., doublets, ^3J(H-H) = 7.6 Hz, with platinum satellites, ^3J(H-Pt) = 24.9 Hz].

Experimental

Infrared spectra were recorded in the 4 000—200 cm^{-1} range on a Perkin-Elmer 1 430 spectrophotometer. Melting points were determined on a Reichert apparatus and are uncorrected. Carbon, H, and N analyses were carried out by the Instituto de Quimica Bio-Organica, Barcelona. The proton n.m.r. spectrum of complex (**4**) ($CDCl_3$ solution, $SiMe_4$ as reference) was recorded on a Varian XL-200 (200 MHz) spectrometer. The mass spectrum of (**1**) was recorded on a Hewlett-Packard GC/MS system 5993 at 70 eV (1.12 × 10^{-17} J). All reactions were carried out at room temperature with magnetic stirring and without special precautions against light, air, or moisture.

[Pt{2-C_6H_4N(O)O}$_2$$Cl_2$] (**1**).—To a red saturated solution of [Pt{2-C_6H_4N(O)O}$_2$][3] (100 mg, 0.23 mmol) in dichloromethane–acetonitrile (10:0.5 cm^3) a saturated solution of chlorine in carbon tetrachloride (10 cm^3) was added. After 6 h the suspension was filtered off and the yellow crystalline solid was washed with dichloromethane (2 × 5 cm^3) to give complex (**1**) in 79% yield, m.p. 274 °C (decomp.) (Found: C, 27.8; H, 1.70; N, 5.30. Calc. for $C_{12}H_8Cl_2N_2O_4Pt$: C, 28.25; H, 1.60; N, 5.50%). Mass spectrum: *m*/*z* 510 (M^+) (36), 439 (M^+ − 2Cl) (100), and 353 (M^+ − $ClC_6H_4NO_2$) (53%). After slow addition of the chlorine solution to a chloroform–acetonitrile solution of the platinum(II) complex, single crystals were obtained when the resulting solution was left to stand for 24 h at room temperature.

[Pt{2-C_6H_4N(O)O}$_2$$X_2$] [X = Br (**2**) *or* I (**3**)].—To a suspension of [Pt{2-C_6H_4N(O)O}$_2$] (0.1—0.2 mmol) in dichloromethane (10 cm^3) the corresponding halogen was added [Br_2 (in excess, *ca.* 21:1) or the stoicheiometric amount of I_2]. After 6 h the resulting solid was filtered off and washed with diethyl ether (2 × 5 cm^3) to give the orange complex (**2**) in 77% yield, m.p. 256 °C (decomp.) (Found: C, 24.2; H, 1.30; N, 4.70. Calc. for $C_{12}H_8Br_2N_2O_4Pt$: C, 24.05; H, 1.35; N, 4.70%) or the red complex (**3**) in 59% yield, m.p. 290 °C (decomp.) (Found: C, 21.2; H, 1.15; N, 4.0. Calc. for $C_{12}H_8I_2N_2O_4Pt$: C, 20.8; H, 1.15; N, 4.05%).

Table 2. Atomic co-ordinates (10^4) for complex (**1**)

Atom	*x*	*y*	*z*
Pt	1 372.6(0.2)	820.8(0.2)	2 438.2(0.1)
Cl(1)	3 100(2)	−587(2)	777(1)
Cl(2)	−375(2)	2 212(2)	4 102(1)
N(1)	−2 123(6)	3 617(6)	1 699(4)
N(2)	3 062(7)	−2 817(5)	3 416(3)
O(1)	−1 415(5)	1 881(5)	1 907(3)
O(2)	1 521(6)	1 797(5)	3 031(3)
O(3)	−3 766(6)	4 499(6)	1 536(4)
O(4)	3 402(7)	−4 360(5)	3 719(4)
C(1)	1 042(7)	3 254(6)	1 812(4)
C(2)	2 399(8)	3 910(7)	1 545(4)
C(3)	1 811(9)	5 698(7)	1 154(5)
C(4)	−116(9)	6 878(7)	1 020(4)
C(5)	−1 465(8)	6 230(7)	1 215(4)
C(6)	−837(7)	4 415(6)	1 593(4)
C(7)	3 813(7)	−262(6)	3 066(4)
C(8)	4 956(8)	512(8)	3 204(5)
C(9)	6 607(8)	−483(9)	3 695(5)
C(10)	7 126(8)	−2 274(8)	4 061(5)
C(11)	5 971(8)	−3 083(8)	3 957(4)
C(12)	4 319(7)	−2 039(7)	3 469(4)

[Pt{2-C_6H_4N(O)O}$_2$Me(I)] (**4**).—To a suspension of [Pt{2-C_6H_4N(O)O}$_2$] (100 mg, 0.23 mmol) in dichloromethane (20 cm^3) was added methyl iodide (1 cm^3). After 6 h the resulting solution was concentrated to 4 cm^3 and n-hexane (15 cm^3) was slowly added to give an orange crystalline solid. This was filtered off and washed with n-hexane (2 × 5 cm^3) to give complex (**4**) in 79% yield, m.p. 169 °C (decomp.) (Found: C, 27.45; H, 1.90; N, 4.90. Calc. for $C_{13}H_{11}IN_2O_4Pt$: C, 26.85; H, 1.90; N, 4.80%).

[Pt{2-$C_6H_4NO_2$}$_2$$Cl_2$(L–L)] [L–L = *phen* (**5**) *or bipy* (**6**)].—To a suspension of complex (**1**) [50 mg, 0.1 mmol in dichloromethane (10 cm^3)] the stoicheiometric amount of the ligand was added. After 6 h the resulting suspension was filtered off and the yellow solid was washed with dichloromethane (2 × 5 cm^3) to give complex (**5**) in 92% yield, m.p. 269 °C (decomp.) (Found: C; 40.95; H, 2.20; N, 7.90. Calc. for $C_{26}H_{16}Cl_2N_2O_4Pt$: C, 41.75; H, 2.35; N, 8.10%) or (**6**) in 72% yield, m.p. 265 °C (Found: C, 39.8; H, 2.35; N, 8.35. Calc. for $C_{22}H_{16}Cl_2N_2O_4Pt$: C, 39.65; H, 2.45; N, 9.40%).

X-Ray Structure Determination of Complex (**1**).—*Crystal data.* $C_{12}H_8Cl_2N_2O_4Pt$, M = 510.2, triclinic, space group $P\bar{1}$, a = 7.922(2), b = 8.172(2), c = 12.531(3) Å, α = 85.60(3), β = 78.84(2), γ = 61.46(2)°, U = 699.0 Å^3, Z = 2, D_c = 2.42 g cm^{-3}, Mo-K_α radiation (λ = 0.710 69 Å), crystal size 0.6 × 0.4 × 0.075 mm, μ = 10.5 mm^{-1}, $F(000)$ = 476.

Data collection and processing. Stoe-Siemens four-circle diffractometer, profile-fitting mode,[12] $2\theta_{max.}$ 55°; 3 824 reflections measured, 3 212 unique (R_{int} 0.022), 3 021 with $F > 4\sigma(F)$ used for all calculations. Absorption correction based on ψ scans (transmissions 0.35—1.00). No crystal decay. Cell constants refined from 2θ values of 58 reflections in the range 20—23°.

Structure solution and refinement. Heavy-atom method. Refinement on F to R 0.028, R' 0.029 [non-H atoms anisotropic, H atoms incorporated using riding model with C–H 0.96 Å, U(H) = 1.2U_{eq}(C); weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,25\,F^2$; 190 parameters]. Program system SHELXTL.[13] Final atomic co-ordinates are given in Table 2.

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