Solvent Extraction of Gold and Platinum-group Metals using 2-Nonylpyridine 1-Oxide, and the Crystal and Molecular Structure of Bis(2-nonylpyridine 1-oxide)hydrogen(1 +) Tetrachloroaurate(III)†

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2-Nonylpyridine 1-oxide (npyo) is a versatile solvent-extraction reagent when dissolved in chloroform. Adjustment of the acid strength (HCl) and reagent concentration can be used to bring about a range of separations. For example, npyo is effective at separating the $[AuCl_4]^-$ ion from other chloro-anions of the platinum-group metals. If required, the $[FeCl_4]^-$ anion may be coextracted at high acid concentration (6 mol dm^{-3} HCl). Chloro-anions of Pt^{IV} can be 90% extracted at npyo concentrations greater than 0.2 mol dm^{-3} in chloroform in a single batch operation. Chloro-anions of Ir^{IV} and Rh^{III} may also be separated. The crystal structure of $[H(npyo)_2][AuCl_4]$ indicates that there are discrete $[AuCl_4]^-$ ions with weak O $\cdots$ Au interactions. Crystals are triclinic, space group $P\bar{1}$, $Z = 4$, with $a = 17.351(11)$, $b = 10.381(9)$, $c = 20.373(8)$ Å, $\alpha = 88.5(1)$, $\beta = 101.8(1)$, and $\gamma = 99.6(1)$°. 4 846 Independent data above background [$I > 3\sigma(I)$] were collected on a diffractometer and the structure refined to R 0.0585. The structure contains two independent $[H(npyo)_2]^+$ cations and one $[AuCl_4]^-$ in general positions and two $[AuCl_4]^-$ ions in special positions with the gold atoms on centres of symmetry. Each $[H(npyo)_2]^+$ cation consists of pairs of npyo ligands associated *via* a hydrogen atom [O $\cdots$ O 2.412(19) and 2.391(16) Å]. The $[AuCl_4]^-$ anions are square planar but two oxygen atoms approach one of the gold atoms in axial positions [3.544(16) and 3.263(15) Å], to provide some weak interaction which may provide a clue to the effectiveness of npyo in the extraction of $[AuCl_4]^-$.

N-Oxides of substituted pyridines and tertiary amines were first proposed as extractants for uranium.[1] 2-Nonylpyridine 1-oxide (npyo) is known to extract Pt^{IV} from dilute nitric or hydrochloric acid solutions for neutron-activation determination of Pt^{IV}.[2] The extraction of mercury(II) chloride by co-ordination of npyo has also been studied. The extracting ability of npyo has been reported to be intermediate between that of $PR(OR)_2O$ and $PR_2(OR)O$ (R = alkyl).[1] Although amine oxides are stronger bases than pyridine *N*-oxides, extraction by them is often complicated by the hydrolysis of the extracted compound in the aqueous phase and this is followed by the subsequent extraction of the products of hydrolysis into the organic phase.[3] Amine oxides gradually degrade in organic solvents to give *N*,*N*-dialkylhydroxylamines. Pyridines are readily oxidised to the *N*-oxides by peracetic acid and have a clear advantage over amine oxides because they do not suffer the same instability problems.

2-Nonylpyridine 1-oxide extracts tantalum selectively from niobium in weak nitric acid solutions but the reverse happens in strong nitric acid solutions. The extraction of fission products including Ta, Nb, and Zr with npyo has been reported.[4] A procedure for separating V and Nb has been developed as V is selectively extracted at pH 2.6—2.8. At low acidities, when amine oxides are weakly protonated, the extractions of U^{VI}, Mo, W, Re, and Co^{II}[3] are more efficient than with amines and a co-ordinative mechanism is possible.

The possibility of using npyo in the extraction of precious metals (Au and Ag), and platinum-group metals (Pd, Pt, Rh, Ir, Ru, and Os) has not been thoroughly studied. The commercial processes involve a 'total' leaching of copper anode slime with chlorine in 5 mol dm^{-3} HCl and Au^{III} may then be extracted using $(BuOCH_2CH_2)_2O$[6] or isobutyl methyl ketone.[7] The acid strength is 5—6 mol dm^{-3} and the metals are present as chloro-anions. The purpose of this research was to investigate whether gold(III) would be selectively extracted by npyo and to obtain detailed information concerning the extracted species. There was also the possibility that the reagent would prove sufficiently versatile to allow separations of the platinum-group metals. There is a particular problem with extractions and separations of Rh^{III} and Ir^{IV} from the platinum(IV) raffinate, the solution which remains after the extraction of Pt^{IV}. It was suggested[7] that Ir^{IV} could be extracted into an amine solvent but problems were encountered with its reduction to Ir^{III} by such solvents and subsequent return of Ir^{III} to the aqueous layer. The ease of packing of organic cations around anions increases from $[MCl_6]^{3-}$ and $[MCl_6]^{2-}$ to $[MCl_4]^{2-}$ and to $[MCl_4]^-$. Consequently, it was thought that species such as $[AuCl_4]^-$, $[PtCl_4]^{2-}$, $[PtCl_6]^{2-}$, and $[IrCl_6]^{2-}$ may be extracted by the $[Hnypo]^+$ cation or its dimer $[H(npyo)_2]^+$, but the extraction of $[RhCl_6]^{3-}$ and $[IrCl_6]^{3-}$ was less likely to occur. Where a co-ordinative mechanism operates (such that the *N*-oxide displaces a chloro- or aquo-group), Pd^{II} and Au^{III} are substitution labile, Ru^{III} and Ru^{IV} are moderately labile, Pt^{II}, Rh^{III}, and Ir^{IV} are moderately inert, and Os^{IV}, Pt^{IV}, and Ir^{III} are inert.[8-11] It was of interest, therefore, to establish whether a co-ordinative mechanism or an ion-pair mechanism was operating for gold(III) which is able to form ion pairs quickly and to undergo rapid ligand substitution. During this work we isolated the compound bis(2-nonylpyridine 1-oxide)hydrogen(1 +) tetrachloroaurate(III) and report its crystal and molecular structure.

Results and Discussion

2-Nonylpyridine 1-oxide (npyo) is less hygroscopic than the 4-nonyl derivative and so is more suitable for solvent-extraction purposes. The extraction data are given in Table 1 using 0.05 mol dm^{-3} npyo in chloroform with different acid (HCl) strengths. These were batch extractions with individual metal-

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† *Supplementary data available* (No. SUP 56142, 11 pp.): thermal parameters, H-atom co-ordinates, cation dimensions. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

ion solutions. The iron(III) ion is increasingly extracted as the HCl molarity increases and the concentration of the $[FeCl_4]^-$ ion increases. Copper(II), Pd$^{\text{II}}$, Pt$^{\text{IV}}$, and Ir$^{\text{IV}}$ are much less well extracted than Au$^{\text{III}}$, of which more than 90% is removed throughout the range of acid concentrations used. Neither Ni$^{\text{II}}$ nor Rh$^{\text{III}}$ was extracted. The previously reported selectivity for Pt$^{\text{IV}}$ [2] was not apparent, at the above concentration of npyo, and is only so at higher concentrations of *N*-oxide. Greater than 90% of the platinum(IV) anion is extracted with concentrations of npyo in excess of 0.2 mol dm^{-3} (Table 2). The extraction figures for the other metals with this higher concentration of *N*-oxide show (Table 3) that more than 90% of Fe$^{\text{III}}$, Pt$^{\text{IV}}$, Ir$^{\text{IV}}$, and Pd$^{\text{II}}$ can be extracted. It is not apparent as to why the figures for Cu$^{\text{II}}$ are so low, but since one of the requirements in precious metal chemistry is to separate these metals from Cu$^{\text{II}}$ the reagent is worth further investigation. The increase in extraction of Fe$^{\text{III}}$ is probably connected with the ion-pair extraction of $[FeCl_4]^-$. The consistently good extraction of the $[PtCl_6]^{2-}$ ion is no doubt connected again with ion-pair association and not substitution. However, for a given reagent concentration, the decrease in extraction of the $[PdCl_4]^{2-}$ ion with increase in acid concentration is intriguing because it would appear that a ligand-substitution reaction operates rather than an ion-pair mechanism. The same is thought to occur with the β-hydroxyoximes.[7] The proposed mechanism which is being further studied is shown in equation (1). The reagent $[H(npyo)_2]^+$ could be at the interface or in the aqueous phase.

Table 1. Percentage extraction for base and precious metals using npyo (0.05 mol dm^{-3}) in chloroform

[HCl]/mol dm^{-3}	Fe$^{\text{III}}$	Cu$^{\text{II}}$	Au$^{\text{III}}$	Pd$^{\text{II}}$	Pt$^{\text{IV}}$	Ir$^{\text{IV}}$
0.1	n.d.	n.d.	93.92	27.1	n.d.	n.d.
1.0	n.d.	n.d.	n.d.	6.19	1.96	1.96
2.0	4.76	1.77	99.40	n.d.	6.54	3.10
4.0	13.04	5.66	98.76	4.76	4.76	2.91
6.0	59.18	4.76	95.30	3.85	n.d.	n.d.
8.0	88.00	2.91	94.59	2.90	3.85	1.96

n.d. = not determined

Table 2. Extraction of platinum(IV) with different concentrations of npyo (initial concentration of H_2PtCl_6 was 0.0125 mol dm^{-3})

[npyo]/mol dm^{-3}	Distribution coefficient (*D*)[a]	% Extraction
0.05	0.05	4.76
0.10	0.52	34.21
0.20	22.86	95.80
0.25	30.61	96.84
0.40	61.22	98.40
0.50	89.50	98.89

[a] For a given metal, M, partitioned between an organic and an aqueous phase *D* = [M(org)]/[M(aq)].

$$[PdCl_4]^{2-}(aq) + [H(npyo)_2]^+ \rightleftharpoons [PdCl_2(npyo)_2]\,(org) + H^+(aq) + 2Cl^-(aq) \quad (1)$$

2-Nonylpyridine 1-oxide seems to have some prospects as a reagent for the commercial separation of Rh$^{\text{III}}$ and Ir$^{\text{IV}}$. The ions $[RhCl_6]^{3-}$ and $[IrCl_6]^{3-}$ or $[IrCl_6]^{2-}$ can coexist. A sufficient supply of chlorine gas can maintain the iridium in the quadrivalent state or the trivalent state can be prepared by addition of a little hydrazine. Whereas both Rh$^{\text{III}}$ and Ir$^{\text{III}}$ have similar extraction curves, that for Ir$^{\text{IV}}$ is quite different and acceptable separations should be possible even at low acid concentrations. Elution of Ir$^{\text{IV}}$ with SO_2–HCl mixtures is being studied as the Ir$^{\text{IV}}$ is reduced to Ir$^{\text{III}}$ which has a reduced affinity for the *N*-oxide.

The affinity of npyo for Au$^{\text{III}}$ is indicated in Table 4. The separation ratios are all high with the exception of Au$^{\text{III}}$/Pd$^{\text{II}}$. In this case the $[AuCl_4]^-$ anion is probably extracted either as an ion pair or as a co-ordination compound. The $[PdCl_4]^{2-}$ ion is probably extracted as a co-ordination compound, although this is being further investigated as is the selective reduction of gold with oxalic acid from the extracted solution in chloroform which contains both Au$^{\text{III}}$ and Pd$^{\text{II}}$.

The separation ratios of npyo for other mixtures of metals in solution are indicated in Table 5. The separation ratio of Pt$^{\text{IV}}$/Ir$^{\text{III}}$ of *ca.* 30 is slightly higher than that (*ca.* 12) which might be expected from Table 3. This could be because the ion pair formed with $[PtCl_6]^{2-}$ (a bivalent ion) is formed more quickly than that with $[IrCl_6]^{3-}$. Some support for this comes from the fact that the separation ratio for Pt$^{\text{IV}}$/Rh$^{\text{III}}$ is over 1 000 after 5 min whereas it is only 19 after 1 h. Clearly the kinetics of separation warrant further investigation. Perhaps a single reagent could be used for the majority of the separations of the platinum-group metals.[12]

*The Structure of the npyo–*Au$^{\text{III}}$ *Compounds.*—Since npyo is efficient at extracting Au$^{\text{III}}$ and separating this from other precious metal anions, it was of interest to see whether the extracted species was solely an ion pair between the protonated *N*-oxide and $[AuCl_4]^-$ or whether there was some degree of covalent binding. Precious metal anions are known to form stable ion pairs and it was of interest to see whether there was some degree of covalency in the ion-pair bond. It was also hoped that a crystal structure might reveal strong hydrophobic interactions between the hydrocarbon chains and quite separate regions of ionic character.

The ^1H n.m.r. spectroscopic data are listed in Table 6. The resonance of the deshielded proton at 9.34 p.p.m. is similar to that attributed to the proton in a symmetrical hydrogen bond in the 2-alkylpyridine 1-oxide dimer in halogeno-acids.[13] In the i.r. spectrum there are no bands between 2 100 and 1 700 cm^{-1}, possibly because the hydrogen bond is symmetrical. The band at 825 cm^{-1} and a weaker one at 1 265 cm^{-1} are attributed to a symmetrical hydrogen bond.[13] The u.v. spectrum showed a

Table 3. Percentage extraction figures for simple metal–ion solutions using 2-nonylpyridine 1-oxide (0.4 mol dm^{-3} in chloroform)

	Fe$^{\text{III}}$		Cu$^{\text{II}}$		Pt$^{\text{IV}}$		Ir$^{\text{IV}}$		Ir$^{\text{III}}$		Rh$^{\text{III}}$		Pd$^{\text{II}}$	
[HCl]/mol dm^{-3}	*D*	%	*D*	%	*D*	%	*D*	%	*D*	%	*D*	%	*D*	%
0.1	—	—	—	—	4.38	81.4	6.79	87.1	—	—	0.01	0.9	39	97.5
1.0	0.13	11.5	—	—	28.5	96.6	40.4	97.6	0.09	8.3	0.06	5.7	18.9	95.0
2.0	10.4	51.0	0.05	4.8	81.3	98.8	50.8	98.1	0.27	21.3	0.22	17.7	—	—
4.0	13.9	93.3	0.15	13.0	61.2	98.4	—	—	—	—	0.05	4.8	22	68.7
6.0	74.8	98.7	0.12	8.6	43.6	97.8	23.3	95.9	0.027	2.6	0.02	1.5	—	—
8.0	147.8	99.3	0.06	5.4	18.7	94.9	16.2	94.0					0.4	27.3

Table 4. Separation ratios between gold(III) and some base and precious metals using npyo (0.05 mol dm^{-3}) in HCl (1 mol dm^{-3})

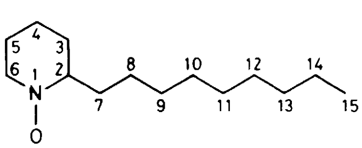
Au^{III}		Other metal ions			
D	%	Ion	*D*	%	$\alpha = \frac{D(Au^{III})}{D(M)}$
479	99.8	Fe^{III}	0.02	2.0	2.4×10^4
522	99.8	Cu^{II}	0.02	1.6	3.2×10^4
1 143	99.9	Pt^{IV}	0.03	2.9	3.8×10^4
215	99.6	Ir^{IV}	0.03	2.6	8.0×10^3
10.6	91.4	Pd^{II}	0.13	11.5	81.5
345	99.7	Rh^{III}	0	0	Infinite

Table 5. Separation ratios between Pt^{IV}, Rh^{III}, and Ir^{III} using npyo (0.4 mol dm^{-3}) in chloroform

Conditions ([HCl]/mol dm^{-3} and *t*/min)	Pt^{IV}		Other metal ions			
	D	%	Ion	*D*	%	$\alpha = \frac{D(Pt^{IV})}{D(M)}$
2, 60	19.7	95.2	Ir^{III}	0.66	39.8	29.9
2, 60	23.3	95.9	Rh^{III}	1.22	35.0	19.1
2, 5	22.7	95.8	Rh^{III}	0.02	2.1	1.14×10^3
4, 60	74.0	88.0	Rh^{III}	0.34	25.1	22.1

Table 6. Proton n.m.r. spectroscopic data for $[H(npyo)_2][AuCl_4]$ in dimethyl sulphoxide

$C_{14}H_{23}NO$	$[H(C_{14}H_{23}NO)_2]^+$	Proton assignment
—	9.34 (1, s)	Deshielded proton (hydrogen bond)
8.32 (1, d)	8.71 (2, d)	C^6 ring
7.42 (3, m)	7.81 (6, m)	C^3—C^5
3.46 (2, t)	3.01 (4, t)	C^7
1.80 (2, br t)	1.75 (4, t)	C^8
1.41 (12, s)	1.33 (24, s)	C^9—C^{14}
1.02 (3, t)	0.93 (6, t)	C^{15}



single maximum at 316 nm (ε 4 800 dm^3 mol^{-1} cm^{-1}) which is akin to that for $[AuCl_4]^-$. This dimer with a proton bridge is quite different from a protonated pyridine derivative as in the latter there can be a rapid proton transfer. This implies that in processes which involve *N*-oxides as solvent-extraction reagents in acidic media an ion-pair mechanism might dominate rather more than with pyridine derivatives.

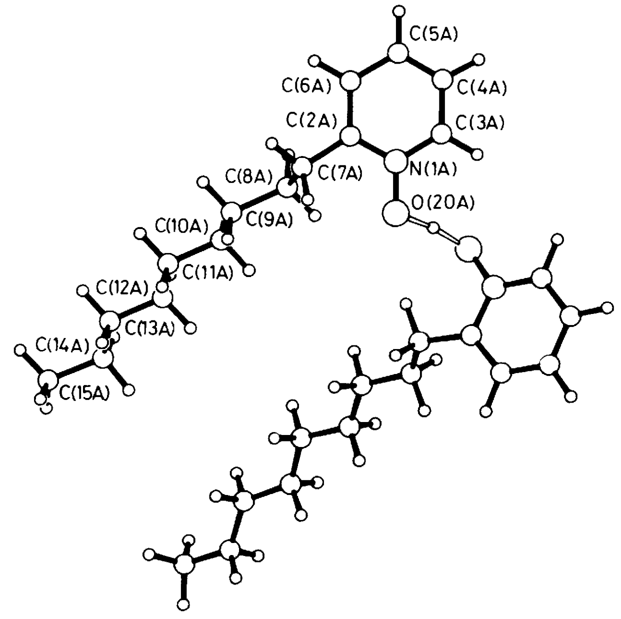


Figure 1. The $[H(npyo)_2]^+$ cation

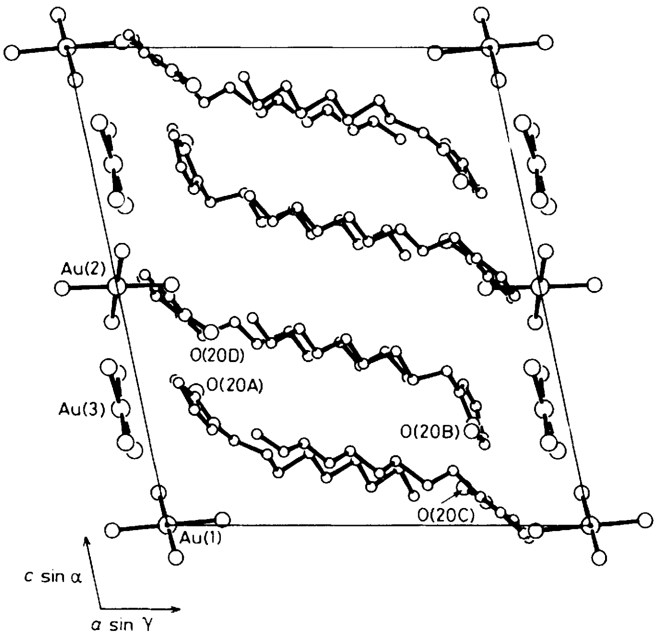


Figure 2. The unit cell of bis(2-nonylpyridine 1-oxide)hydrogen(1+) tetrachloroaurate(III) in the *b* projection

$[H(npyo)_2][AuCl_4]$. The asymmetric unit contains two independent $[H(npyo)_2]^+$ cations and one $[AuCl_4]^-$ in general positions, and two $[AuCl_4]^-$ in special positions with the gold atoms situated on centres of symmetry. Each $[H(npyo)_2]^+$ cation consists of pairs of 2-nonylpyridine 1-oxide ligands associated *via* a hydrogen atom. The two O ··· O distances are very short, O(20A) ··· O(20D) 2.412(19) and O(20B) ··· O(20C) 2.391(16) Å, values which confirm that the hydrogen atom must be positioned between the two oxygen atoms (Figure 1). After the refinement was completed a Fourier difference synthesis was calculated and we searched for the hydrogen atoms between the oxygen atoms. These were unambiguously located, but the positions could, however, not be refined and we were unable to establish whether the hydrogen bonds are symmetrical. In bis(pyridine 1-oxide)hydrogen(1+) tetrachloroaurate(III),[14] the O ··· O distance is 2.41(1) Å and a symmetrical hydrogen bond is assumed. In the present structure the i.r. spectrum suggests that symmetrical hydrogen bonds are present, and the O ··· O distances are sufficiently short to support this hypothesis. Of the three $[AuCl_4]^-$ anions, two are perforce planar and indeed so is the anion in general positions within experimental error. The independent Au–Cl bond lengths range from 2.256(5) to 2.306(5) Å. Angles subtended at the metal are all within 2.1° of the expected values for an ideal square-planar arrangement. The Au–Cl bond lengths are comparable with those found in other $[AuCl_4]^-$ anions. The Cambridge Data Centre files revealed only eight examples of this anion. The mean Au–Cl distance is 2.272 Å with a spread from 2.258 to 2.291 Å.

Figure 2 illustrates the packing of the molecules in the *b* projection. As can be seen there are layers of anions along the *c* axis. The aliphatic chains are approximately parallel to the *a* direction.

It is interesting to investigate whether there is any interaction between *the* $[AuCl_4]^-$ anions and the cations. As can be seen from Figure 1 there is no contact with the anions in special positions but there are two contacts involving Au(3), namely Au(3) ··· O(20A) 3.544(16) and Au(3) ··· O(20B) 3.263(15) Å. We suggest that it is significant that the oxygen atoms in the cation are closest to the metal and that this represents some weak interaction. The O–Au–Cl angles are all within 15° of perpendicular. The arrangement about Au(3) is illustrated in Figure 3.

Of the other structures containing $[AuCl_4]^-$ in the Cambridge Data Centre files, only two had a weak interaction in the axial direction, *viz.* in bis(pyridine 1-oxide)hydrogen(1+) tetrachloroaurate(III)[14] there are two Au ··· O distances of 3.107 Å and in 2,2-dimethyl-2*H*-benzimidazole 1,3-dioxide oxonium tetrachloroaurate(III)[15] the Au ··· O distances are 3.181 Å. In each of these structures, discrete planar $[AuCl_4]^-$ anions can be detected. There does appear to be some weak Au ··· O interaction but the dominant mode of action is by an ion-pair mechanism.

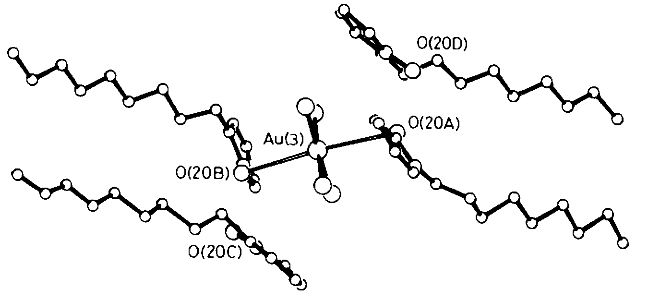


Figure 3. The arrangement of two $[H(npyo)_2]^+$ cations about an $[AuCl_4]^-$ anion

Conclusions

The reagent 2-nonylpyridine 1-oxide is a versatile one which can be used for the extraction of precious metals and warrants further investigation. The data obtained suggest than an ion-pair mechanism operates for extraction of Au^{III}.

Experimental

2-Nonylpyridine 1-oxide was prepared by oxidation of the corresponding pyridine compound with peracetic acid (Found: C, 74.25; H, 10.5; N, 6.30. $C_{14}H_{23}NO$ requires C, 75.95; H, 10.45; N, 6.35%). Bis(2-nonylpyridine 1-oxide)hydrogen(1+) tetrachloroaurate(III) was prepared by dissolving npyo (1.13 g, 5.2

Table 7. Atomic co-ordinates (10^4) with estimated standard deviations in parentheses for $[H(npyo)_2][AuCl_4]$

Atom	*x*	*y*	*z*
Au(1)	0	0	0
Au(2)	0	0	5 000
Au(3)	13(1)	5 687(1)	2 440(1)
Cl(1)	166(4)	−1 642(5)	5 763(3)
Cl(2)	1 331(3)	443(5)	5 038(3)
Cl(3)	126(3)	1 782(4)	683(2)
Cl(4)	1 339(3)	300(5)	111(3)
Cl(5)	273(3)	7 429(5)	3 173(2)
Cl(6)	−238(4)	3 926(5)	1 722(3)
Cl(7)	−228(4)	4 353(5)	3 316(3)
Cl(8)	246(3)	7 035(5)	1 560(2)
O(20A)	1 785(9)	4 302(12)	2 829(7)
N(1A)	1 587(10)	2 953(16)	2 692(8)
C(2A)	1 834(13)	2 505(21)	2 167(10)
C(3A)	1 157(13)	2 166(22)	3 081(11)
C(4A)	979(13)	904(20)	2 946(11)
C(5A)	1 270(15)	343(24)	2 429(12)
C(6A)	1 660(14)	1 165(23)	2 026(10)
C(7A)	2 302(21)	3 528(24)	1 766(12)
C(8A1)	3 014(28)	3 759(43)	1 942(22)
C(8A2)	2 906(33)	3 028(54)	1 377(26)
C(9A)	3 321(15)	4 373(33)	1 188(17)
C(10A)	4 137(15)	5 023(25)	1 513(12)
C(11A)	4 554(14)	5 854(27)	1 021(12)
C(12A)	5 355(14)	6 637(27)	1 340(13)
C(13A)	5 749(18)	7 528(30)	814(15)
C(14A)	6 515(18)	8 388(30)	1 126(17)
C(15A)	6 827(16)	9 200(31)	630(17)
O(20B)	−1 730(9)	6 592(13)	1 976(5)
N(1B)	−1 539(9)	7 866(16)	2 145(8)
C(2B)	−1 634(11)	8 252(19)	2 759(10)
C(3B)	−1 449(12)	9 598(24)	2 931(10)
C(4B)	−1 141(13)	10 531(21)	2 482(11)
C(5B)	−1 079(13)	10 123(20)	1 874(10)
C(6B)	−1 273(10)	8 783(16)	1 712(9)
C(7B)	−1 931(13)	7 232(18)	3 223(9)
C(8B)	−2 823(14)	6 854(20)	3 046(10)
C(9B)	−3 171(14)	5 956(29)	3 599(11)
C(10B)	−4 043(15)	5 394(26)	3 361(12)
C(11B)	−4 377(16)	4 545(29)	3 879(12)
C(12B)	−5 221(16)	3 849(27)	3 575(13)
C(13B)	−5 606(20)	3 003(29)	4 075(13)
C(14B)	−6 413(17)	2 226(31)	3 794(15)
C(15B)	−6 814(18)	1 432(35)	4 322(17)
O(20C)	−2 204(9)	6 249(15)	778(6)
N(1C)	−1 871(10)	5 353(18)	500(7)
C(2C)	−2 106(13)	4 052(22)	617(9)
C(3C)	−1 816(15)	3 206(20)	256(9)
C(4C)	−1 308(13)	3 587(21)	−169(10)
C(5C)	−1 056(11)	4 892(20)	−255(9)
C(6C)	−1 359(11)	5 764(18)	78(9)
C(7C)	−2 650(20)	3 702(32)	1 085(15)
C(8C)	−3 373(17)	3 007(31)	861(12)
C(9C)	−3 994(21)	2 557(35)	1 257(16)
C(10C)	−4 633(19)	1 575(34)	1 098(14)
C(11C)	−5 197(17)	1 131(27)	1 502(13)
C(12C)	−5 831(22)	46(38)	1 318(16)
C(13C)	−6 408(18)	−528(32)	1 686(14)
C(14C)	−7 029(24)	−1 715(35)	1 547(18)
C(15C)	−7 570(23)	−2 223(36)	1 911(17)
O(20D)	2 414(9)	4 533(14)	4 018(7)
N(1D)	1 993(9)	5 012(17)	4 391(8)
C(2D)	1 983(12)	6 298(22)	4 375(9)
C(3D)	1 524(15)	6 753(23)	4 792(11)
C(4D)	1 110(16)	5 898(30)	5 185(11)
C(5D)	1 165(17)	4 569(31)	5 182(12)
C(6D)	1 581(16)	4 185(24)	4 784(13)
C(7D)	2 429(14)	7 154(20)	3 944(11)
C(8D)	3 328(15)	7 420(23)	4 257(11)
C(9D)	3 807(17)	8 151(25)	3 761(13)
C(10D)	4 687(16)	8 623(29)	4 045(13)
C(11D)	5 147(20)	9 400(32)	3 547(14)
C(12D)	5 952(21)	10 056(35)	3 843(15)
C(13D)	6 313(19)	10 804(40)	3 336(18)
C(14D)	7 032(28)	11 606(39)	3 574(18)
C(15D)	7 488(20)	12 498(38)	3 071(21)

Table 8. Molecular dimensions in the anions (distances in Å, angles in °)

Cl(3)–Au(1)	2.298(5)	Cl(4)–Au(1)–Cl(3)	89.7(2)
Cl(4)–Au(1)	2.256(5)	Cl(2)–Au(2)–Cl(1)	91.0(2)
Cl(1)–Au(2)	2.291(5)	Cl(6)–Au(3)–Cl(5)	179.1(2)
Cl(2)–Au(2)	2.264(6)	Cl(7)–Au(3)–Cl(5)	87.9(2)
Cl(5)–Au(3)	2.301(5)	Cl(7)–Au(3)–Cl(6)	91.3(2)
Cl(6)–Au(3)	2.298(5)	Cl(8)–Au(3)–Cl(5)	91.9(2)
Cl(7)–Au(3)	2.293(6)	Cl(8)–Au(3)–Cl(6)	88.8(2)
Cl(8)–Au(3)	2.306(5)	Cl(8)–Au(3)–Cl(7)	179.5(2)
O(20A) ··· Au(3)	3.544(16)	O(20A)–Au(3)–Cl	103.5(2), 75.8(2), 78.8(3), 101.6(3)
O(20B) ··· Au(3)	3.263(15)	O(20B)–Au(3)–Cl	83.9(3), 96.7(3), 99.5(3), 80.1(3)

mmol) in ethanol (25 cm^3) and adding to a solution of hydrogen tetrachloroaurate(III) (0.87 g, 2.6 mmol) in 1 mol dm^{-3} hydrochloric acid. The resulting yellow solid was recrystallised from alcohol (Found: C, 43.05; H, 5.65; Au, 25.1; N, 3.60. $C_{28}H_{47}AuCl_4N_2O_2$ requires C, 43.0; H, 6.05; Au, 25.15; N, 3.60%).

Extraction Experiments.—The uptake of metal ions by npyo was determined by measurement of the metal-ion concentration in the aqueous layer by atomic absorption spectrometry using a Perkin-Elmer 272 instrument. The npyo–chloroform solution (20 cm^3) was added to the aqueous metal-containing solution (20 cm^3; 0.0125 mol dm^{-3} metal) which had been adjusted to the required pH or acid concentration. The mixture was shaken for 1 h in a pear-shaped separating funnel (100 cm^3). After this period the phases were allowed to separate and the aqueous phase was run off and analysed for its metal content.

Crystals were prepared by recrystallisation from methanol.

Crystallography.—*Crystal data.* $C_{28}H_{47}AuCl_4N_2O_2$, M = 776.1, triclinic, a = 17.351(11), b = 10.381(9), c = 20.373(8) Å, α = 88.5(1), β = 101.8(1), γ = 99.6(1)°, U = 3 541.4 Å^3, D_m = 1.46, Z = 4, D_c = 1.46 g cm^{-3}, $F(000)$ = 1 556, λ = 0.7107 Å, μ = 46.0 cm^{-1}. The space group was established as $P\bar{1}$ by the successful structure determination.

A crystal of approximate size 0.05 × 0.40 × 0.90 mm was mounted so as to rotate about the a axis on a Stoe STADI2 two-circle diffractometer and data were collected *via* variable-width ω scans. Background counts were of 20 s and the scan rate of 0.033° s^{-1} was applied to a width of (1.5 + sin μ/tan θ). 7 808 Independent reflections were measured of which 4 846 with $I > 3\sigma(I)$ were used in subsequent calculations. An absorption correction was applied using SHELX 76.[16] Minimum and maximum transmission factors were 0.787 and 0.063.

The positions of the three independent gold atoms were obtained from the Patterson function. Two were in special positions situated on centres of symmetry at 0,0,0 and 0,0,$\frac{1}{2}$ respectively. Further Fourier calculations gave the positions of the remaining non-hydrogen atoms which were then refined anisotropically. Hydrogen atoms bonded to carbon were included in tetrahedral or trigonal positions. Hydrogen atoms in each ring, of the methylene groups of each aliphatic chain, and of each methyl group were given common thermal parameters. The structure was then refined by full-matrix least squares using SHELX 76[16] to R = 0.0585 (R' 0.0603). The weighting scheme was chosen to give equivalent values of $w\Delta^2$ over ranges of F_o and (sin θ)/λ. This was $w = 1/[\sigma^2(F) + 0.003F^2]$ with $\sigma(F)$ taken from counting statistics. Scattering factors were taken from ref. 17.

Calculations were made using SHELX 76 on the CDC 7600 computer at the University of Manchester Computer Centre. Atomic co-ordinates are listed in Table 7, interatomic distances and angles in Table 8.

Acknowledgements

L. R. G. thanks London and Scandinavian Metal Co. and the S.E.R.C. for financial support. John Barnes at INCO is thanked for advice concerning Platinum Group Metal processing. Johnson Matthey Chemicals are thanked for supplying the gold compounds. We also thank A. W. Johans for his assistance with the crystallographic investigations.

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Received 15*th June* 1984; *Paper* 4/1010