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TWO NEW COMPLEXES OF 1,8-NAPHTHYRIDINE (napy): THE X-RAY CRYSTAL STRUCTURES OF $[OsO_4(napy)]$ (1) AND OF $[Ag_2(\mu\text{-napy})_2(NO_3)_2]$ (2)

WILLIAM P. GRIFFITH,* TSE YUEN KOH, ANDREW J. P. WHITE
and DAVID J. WILLIAMS*

Chemical Crystallographic and Inorganic Chemistry Research Laboratories,
Department of Chemistry, Imperial College of Science, Technology and Medicine,
London SW7 2AY, U.K.

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Abstract—The X-ray crystal structures of the title complexes are reported together with their Raman spectra. In **1**, 1,8-naphthyridine is monodentate, occupying an axial position of a trigonal bipyramid; in **2** the ligand adopts a bidentate bridging mode binding two $Ag(NO_3)$ units. Vibrational spectra of **1** and **2** are also compared with that of the free ligand.

X-Ray crystallographic analyses have shown that the ligand 1,8-naphthyridine coordinates to metals in three ways: bidentate, monodentate and binuclear bridging. Bidentate complexes tend to have high coordination numbers because of the small bite of the ligand. Homoleptic *tetrakis* species have been reported for most of the first row transition metals as perchlorate salts,[1] and the X-ray crystal structures of the dodecahedral complex $[Fe(napy)_4](ClO_4)_2$[2] and of $[Cd(napy)_4](ClO_4)_2$[3] have been described. Monodentate 1,8-naphthyridine appears to be less common but has been found in the dimercury (I) complex $[Hg_2(napy)_2]^{2+}$, although in this structure there is some interaction from the other nitrogen atom.[4] The ligand is also monodentate in $[Cu(napy)_2Cl_2]$.[5] Complexes with bridging binuclear 1,8-naphthyridine include $[Cu_2(\mu\text{-napy})_2Cl_4]$,[6] and the mixed valence complex $[Ni_2(\mu\text{-napy})_4Br_2]$.[7] Both $[Ag_2(\mu\text{-napy})_2(ClO_4)_2]$[8,9] and $[Cu_2(\mu\text{-napy})_2(ClO_4)_2]$[8] have also been recently characterized by X-ray diffraction.

We have been interested in measuring the Surface Enhanced Raman Spectra (SERS) of a number of bidentate O,O′ and O,N′ donors[10] and N,N′ donors[11] on silver colloids with the aim of establishing the orientation of these molecules at the metal surfaces. For this work it has been of value to measure also the conventional Raman spectra of metal complexes of such ligands, since they provide models for a configuration of the ligand which is perpendicular ("edge-on") to the metal surface.[9] We found that 1,8-naphthyridine gave excellent SERS on silver colloids down to a concentration of as low as 10^{-4} M, and in order to help us interpret these results we have prepared a number of known and new metal complexes of the ligand. During the course of this work we isolated the two title complexes and report here their X-ray crystal structures together with their Raman spectra.

RESULTS AND DISCUSSION

X-Ray crystal structure of $[OsO_4(napy)]$

The osmium adduct (**1**) was obtained as yellow blocky needles by reacting OsO_4 and 1,8-naphthyridine in CCl_4. When isolated, the adduct decomposes in air over a period of several hours to give a black residue, although it is sufficiently stable for its Raman spectrum to be measured.

The X-ray structure shows the osmium atom to be coordinated to one naphthyridine and four oxo ligands in a distorted trigonal bipyramidal

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* Authors to whom correspondence should be addressed.

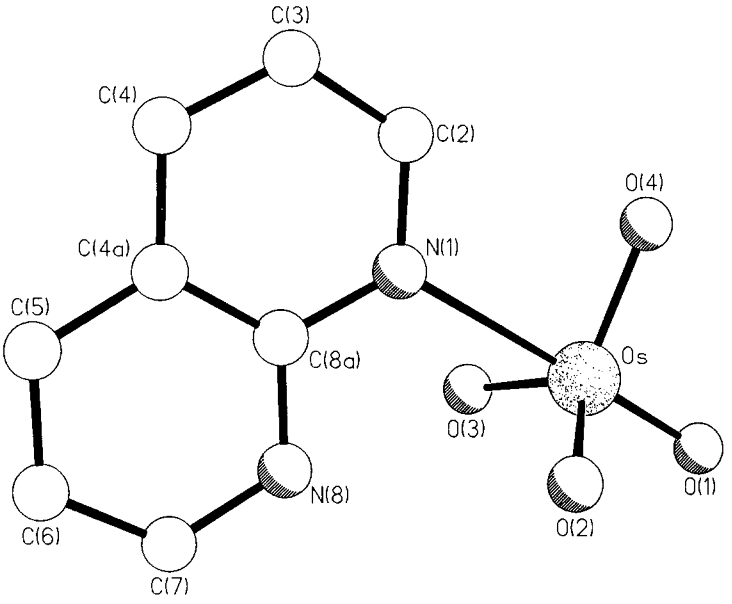

Fig. 1. X-Ray crystal structure of $[OsO_4(napy)]$ (**1**).

geometry with the nitrogen atom of the monodentate naphthyridine occupying one of the axial positions (Fig. 1). The Os—O distances are in the range 1.701(7) [O(1)] to 1.722(7) Å [O(4)] (Table 1) similar to those reported for OsO_4 in the gas phase (1.711(3) Å).[12] The Os—N bond distance [2.438(6) Å] is long (*cf.* normal Os—py distances of 2.17 Å),[13] but comparable with those reported for $[OsO_4(quinuclidine)]$ and $[(OsO_4)_2HMTA]$ (HMTA = hexamethylenetetraamine), the only other structurally characterized examples of N-adducts of OsO_4.[14] The O(1)—Os—N(1) angle is essentially linear at 178.4(3)°; however, the three equatorial oxygen atoms, O(2), O(3) and O(4), are all appreciably bent away from the axial oxygen atom [average O(1)—Os—O_{eq} angle 102°], the osmium atom lying 0.34 Å out of the plane of these three oxygen atoms. Thus the OsO_4 unit still retains much of its original tetrahedral character. The naphthyridine ligand itself is planar to within 0.01 Å and coplanar with O(1), Os and O(4) [the C(2)—N(1)—Os—O(4) torsion angle is 4°], there being a fairly strong C—H···O hydrogen bond between the *ortho* proton attached to C(2) and the equatorial oxygen O(4) [H···O distance 2.28 Å, C—H···O angle 114°].

The molecules pack with the naphthyridine rings oriented parallel and overlapping to form π–π stacks that extend in the crystallographic *a* direction. The interplanar separations are 3.64 and 3.69 Å (Fig. 2).

Table 1. Selected bond lengths (Å) and angles (°) for $[OsO_4(napy)]$ (with e.s.d.s in parentheses)

Os—O(1)	1.701(7)		
Os—O(2)	1.710(6)		
Os—O(3)	1.706(6)		
Os—O(4)	1.722(7)		
Os—N(1)	2.438(6)		
O(1)—Os—O(2)	102.0(4)	O(1)—Os—O(3)	100.7(4)
O(2)—Os—O(3)	116.1(3)	O(1)—Os—O(4)	102.1(4)
O(2)—Os—O(4)	114.8(4)	O(3)—Os—O(4)	117.3(4)
O(1)—Os—N(1)	178.4(3)	O(2)—Os—N(1)	78.7(3)
O(3)—Os—N(1)	77.6(2)	O(4)—Os—N(1)	78.9(3)

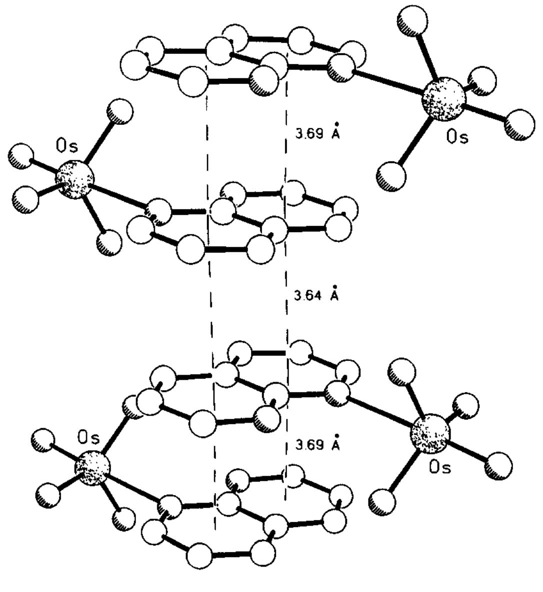

Fig. 2. Part of one of the napy–napy π–π stacks in the crystal structure of **1**.

X-Ray crystal structure of $[Ag_2(\mu\text{-napy})_2(NO_3)_2]$

The silver (I) complex (**2**) was prepared by reacting $AgNO_3$ with 1,8-naphthyridine in water and crystallized to produce clear prisms suitable for X-ray analysis.

The X-ray structure (Fig. 3) shows the complex to be binuclear with a pair of naphthyridine ligands adopting a bidentate bridging coordination mode to the two silver centres; each silver also coordinates a bidentate nitrate. The geometry of the complex is very similar to those reported by Munakata *et al.*[8] and Tsuda *et al.*[9] for the perchlorate analogue $[Ag_2(\mu\text{-napy})_2(ClO_4)_2]$. The complex has crystallographic C_i symmetry and the two independent Ag—N bond lengths are within statistical significance identical: 2.204(3) Å, N(8′) and 2.213(3) Å, N(1) (Table 2). If one considers NO_3^- as a monodentate ligand occupying only one coordination site then the coordination geometry about the silver atom can be described as distorted square planar with angles in the range 83.3–97.8°.

The Ag—NO_3^- bonds are asymmetric with Ag—O bond lengths of 2.59 and 2.64 Å, with the longer bond being almost *trans* to the Ag—Ag′ vector [bond angle O(22)—Ag—Ag′ 172.8(1)°]. In $[Ag_2(\mu\text{-napy})_2(ClO_4)_2]$ the Ag—O distance to the coordinated perchlorate is similar at 2.64 Å. In both structures there is an appreciable departure from linearity for the N—Ag—N angle, 164.8(1)° in **2** (*cf.* 167.8° in the perchlorate complex). These distortions are thought to be a consequence of the secondary coordination between the metal and the oxyanions.[8] There is probably a weak interaction between the two silver atoms [Ag—Ag′ 2.780(1) Å]—this distance is longer than in the perchlorate complex [2.748 Å][8] but shorter than the silver–silver separation in the bulk metal (2.889 Å).[15] Shorter silver–silver distances are known (down to 2.654 Å)[16] and it has been postulated that the inter-metal distance in, for example, silver dithiocarbamate complexes is determined primarily by ligand geometry.[17] The silver atoms are also displaced out of the plane of the four nitrogen atoms by 0.20 Å, one on either side of the plane. As with the osmium complex (**1**), the naphthyridine rings are coplanar, here to within 0.04 Å.

There is a chain of Ag–$p\pi$ interactions between adjacent molecules that extend through the crystal (Fig. 4). The distance between a silver atom and the centre of one of the π rings of the neighbouring naphthyridine is 3.5 Å. The Ag—napy ring centroid vector is inclined by 75° to the plane of the ring.

Vibrational spectra of naphthyridine complexes

The vibrational spectrum of 1,8-naphthyridine has been fully assigned by Carrano *et al.*[18] and we have used their assignments here.

Raman spectra of the free ligand and data for **1** and $[Cu(napy)_2Cl_2]$ (in which the ligand is also known to be monodentate), and for **2** and $[Cu_2(\mu\text{-napy})_2(\mu\text{-Cl})_2Cl_2]$ are listed in Table 3. The aim is to establish whether such spectra can be used to distinguish bonding modes of 1,8-naphthyridine. It

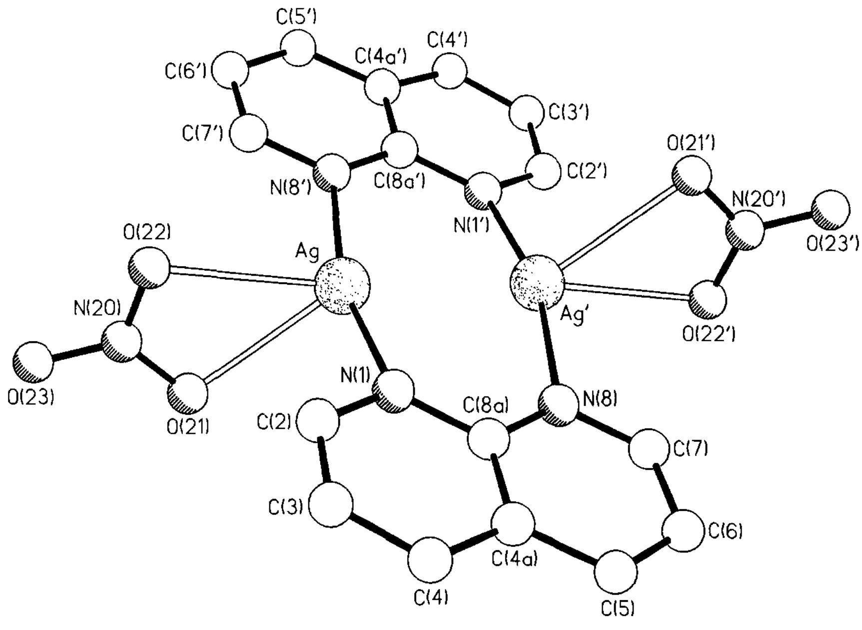

Fig. 3. Perspective view of $[Ag_2(\mu\text{-napy})_2(NO_3)_2]$ (**2**).

Table 2. Selected bond lengths (Å) and angles (°) for [$Ag_2(\mu\text{-napy})_2(NO_3)_2$] (with e.s.d.s in parentheses)

Ag—N(1)	2.213(3)		
Ag—O(21)	2.592(3)		
Ag—Ag′	2.780(1)		
Ag—N(8′)	2.204(3)		
Ag—O(22)	2.643(3)		
O(21)—Ag—N(8′)	103.5(1)	N(1)—Ag—O(21)	91.6(1)
Ag′—Ag—N(8)	84.4(1)	O(21)—Ag—Ag′	140.1(1)
N(1)—Ag—N(8′)	164.8(1)	Ag′—Ag—O(22)	172.8(1)
O(22)—Ag—N(8′)	94.4(1)	Ag′—Ag—N(1)	83.3(1)
O(21)—Ag—O(22)	47.1(1)	N(1)—Ag—O(22)	96.8(1)

is readily appreciated from Table 3 that although there is no clear distinction between monodentate and bidentate coordination, the spectra of the free ligand and **1** are very similar as might be expected in view of the weak interaction between OsO_4 and the ligand. Strong bands in the Raman at 949, 928 and 909 cm^{-1}, and 380, 342, 305 and 298 cm^{-1}, which are not present in the spectrum of the free ligand, clearly arise from the OsO_4 moiety (similar features have been noted for other amine adducts of OsO_4).[19] In **2** where the ligand is bidentate and bridging, the prominent bands in the Raman of the free ligand at 536, 760 and 1049 cm^{-1} are all shifted upwards in wavenumber by 10–30 cm^{-1}. The intensities of the bands in the spectra of the copper complexes are quite different, presumably because of the stronger ligand–metal interaction here. Nevertheless the spectra of **2**, [$Cu(napy)_2Cl_2$] and [$Cu_2(\mu\text{-napy})_2(\mu\text{-Cl})_2Cl_2$] have some common features, e.g. there is only one band at 1420 cm^{-1} while in the free ligand and **1** there are two bands of equal intensity in this region.

EXPERIMENTAL

1,8-Naphthyridine was obtained from Aldrich Ltd and was used without purification.

Preparation of [$Ag_2(\mu\text{-napy})_2(NO_3)_2$]

Silver nitrate, $AgNO_3$ (0.0173 g, 0.1 mmol), dissolved in water (0.5 cm^3) was added to 1,8-naphthyridine (0.013 g, 0.1 mmol) in ethanol (0.5 cm^3) to give a white amorphous solid. This was left in the dark for 2 days to give white crystals which were filtered, washed with water, ethanol and ether. Found: C, 32.1; H, 1.9; N, 13.9. Calc. for $C_8H_6N_3O_3Ag$: C, 32.0; H, 2.0; N, 14.0%.

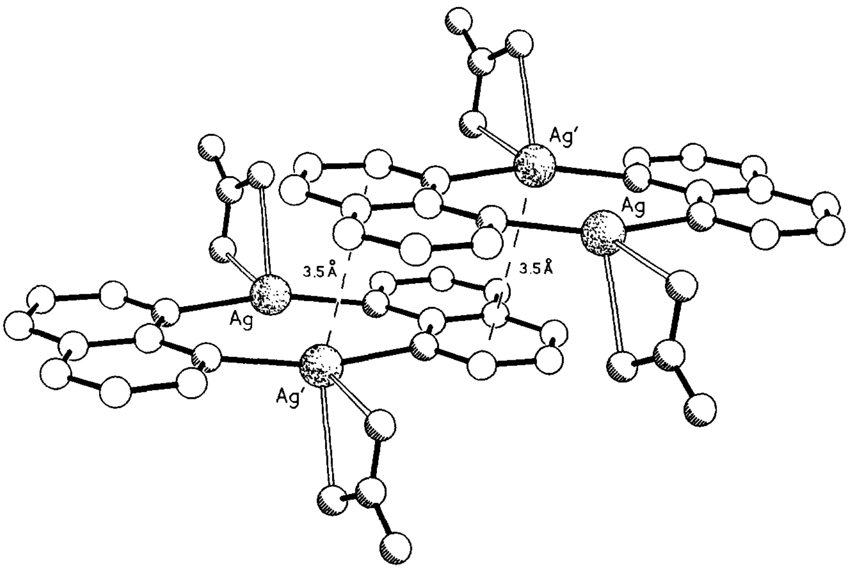

Fig. 4. Part of the extended stepped Ag–*pπ* interactions present in the structure of **2**.

Table 3. Raman spectra of complexes of 1,8-naphthyridine (napy) (cm^{-1})

(napy)	$[OsO_4(napy)]$	$[Ag_2(\mu\text{-}napy)_2(NO_3)_2]$	$[Cu_2(napy)_2Cl_4]$	$[Cu(napy)_2Cl_2]$	Assignments[18]
1600w	1603w	1605(2)	1606(1)	1602(2)	νCC
1560(4)	1576(1)	1566(2)	1570(2)	1575(2)	νCC
1417(4)	1421(1)	1420(1)	1416(1)	1420(5)	νCC
1395(4)	1391(1)	1396sh			νCC
	1372(1)				
1362(10)	1362(2)	1365(10)	1348(10)	1382(10)	νCC
1329vw		1330(1)	1332(4)		
1294w	1300w	1293(1)	1294(1)	1301(1)	νCC
		1274vw			νNO_3
1229w	1232w	1239w	1242(3)		νCC
1127(1)	1140(1)	1139(1)	1142(2)	1138(2)	δCH
1049(4)	1066(1)	1069(2)	1084(2)	1059(4)	νCC
		1031(5)			νNO_3
	949(1)				νOsO_4
	928(10)				νOsO_4
	909(6)				νOsO_4
760(6)	774(3)	787(5)	792(3)	787(5)	νCC
536(3)	543(2)	546(3)	546(3)	548(4)	νCC
397(1)		413(1)		410(1)	
	380(5)				δOsO_4
	352(1)				δOsO_4
	305(3)				δOsO_4
	298(3)				δOsO_4
				296(1)	$\nu CuCl$
				245(1)	$\nu CuCl$

For $[Cu_2(napy)_2Cl_4]$, $\lambda_o = 514.5$ nm and for the others, $\lambda_o = 1064$ nm. All samples run as solids.

Preparation of $[OsO_4(napy)]$

Osmium (VIII) tetraoxide, OsO_4 (0.0527 g, 0.2 mmol), was dissolved in 3 cm^3 CCl_4 (Analar grade). To this solution was added 1,8-naphthyridine (0.054 g, 0.4 mmol) which dissolved slowly over the course of a day to produce a yellow solution. When all the solid had dissolved, the mixture was kept at 4°C for a week until orange crystals were formed.

Preparation of $[Cu(napy)_2Cl_2]$

This was made by the literature method.[20] Copper (II) chloride dihydrate, $CuCl_2 \cdot 2H_2O$ (0.017 g, 0.1 mmol), was dissolved in water (1 cm^3) and added to an aqueous solution of 1,8-naphthyridine (0.026 g, 0.2 mmol in 2 cm^3). The green solution was left to evaporate slowly to yield green crystals. Found : C, 48.5 ; H, 3.0 ; N, 14.1. Calc. for $C_{16}H_{12}N_4CuCl_2$: C, 48.7 ; H, 3.1 ; N, 14.2%.

Preparation of $[Cu_2(\mu\text{-}napy)_2(\mu\text{-}Cl)_2Cl_2] \cdot H_2O$

This was made by the literature method.[6] Copper (II) chloride dihydrate, $CuCl_2 \cdot 2H_2O$ (0.017 g, 0.1 mmol), was dissolved in 95% ethanol (2 cm^3), heated to 70°C. 1,8-Naphthyridine (0.013 g, 0.1 mmol) was added and the green solution cooled to room temperature. The precipitate was filtered and washed with 95% ethanol. Found : C, 35.5 ; H, 2.1 ; N, 10.2. Calc. for $C_{16}H_{12}N_4Cu_2Cl_4$: C, 35.1 ; H, 2.6 ; N, 10.2%.

$[OsO_4(napy)]$

*Crystal data.** $C_8H_6N_2O_4Os$, $M = 384.3$, monoclinic, $a = 7.265(2)$, $b = 10.639(2)$, $c = 12.826(2)$ Å, $\beta = 100.40(2)°$, $V = 975.0(2)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 2.618$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.71073$ Å, μ(Mo-K_α) = 131 cm^{-1}, $F(000) = 704$.

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* Tables of atomic positional and thermal parameters have been deposited as Supplementary Data with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

Measurements. Data were measured on a Siemens P4/PC diffractometer with Mo-K_α radiation (graphite monochromator) using ω scans. A crystal of dimensions $0.27 \times 0.33 \times 0.50$ mm coated in epoxy resin to prevent decomposition was used; 1717 independent reflections were measured ($2\theta \leqslant 45^\circ$), of which 1469 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors and an empirical absorption correction was applied—the maximum and minimum transmission factors were 0.399 and 0.092 respectively.

Structure analysis and refinement. The structure was solved by the heavy-atom method and the non-hydrogen atoms refined anisotropically. The positions of the hydrogen atoms were idealised, C—H = 0.96 Å, assigned isotropic thermal parameters, $U(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{C})$ and allowed to ride on their parent carbons. Refinement was by full-matrix least-squares to give $R = 0.033$, $R_w = 0.035$ [$w^{-1} = \sigma^2(F) + 0.0007F^2$]; the maximum and minimum electron densities in the final ΔF map were 1.04 and -0.97 eÅ^{-3} respectively. Computations were carried out on a 50 MHz 486 PC using the SHELXTL PC program system.[21]

$[\mathrm{Ag_2(\mu\text{-}napy)_2(NO_3)_2}]$

Crystal data. $C_{16}H_{12}Ag_2N_6O_6$, $M = 600.1$, triclinic, $a = 5.818(2)$, $b = 8.635(2)$, $c = 10.036(2)$ Å, $\alpha = 66.48(2)$, $\beta = 86.65(2)$, $\gamma = 77.64(2)^\circ$, $V = 451.4(1)$ Å^3, space group $P\bar{1}$, $Z = 1$, $D_c = 2.207$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo-}K_\alpha) = 22$ cm^{-1}, $F(000) = 292$.

Measurements. Data were measured on a Siemens P4/PC diffractometer with Mo-K_α radiation (graphite monochromator) using ω scans. A crystal of dimensions $0.13 \times 0.17 \times 0.20$ mm was used; 2553 independent reflections were measured ($2\theta \leqslant 45^\circ$), of which 2106 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors and a semi-empirical absorption correction was applied—the maximum and minimum transmission factors were 0.638 and 0.544 respectively.

Structure analysis and refinement. The structure was solved by the heavy-atom method and the non-hydrogen atoms refined anisotropically. The positions of the hydrogens atoms were idealised, C—H = 0.96 Å, assigned isotropic thermal parameters, $U(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{C})$ and allowed to ride on their parent carbons. Refinement was by full-matrix least-squares to give $R = 0.030$, $R_w = 0.034$ [$w^{-1} = \sigma^2(F) + 0.0007F^2$]; the maximum and minimum electron densities in the final ΔF map were 0.63 and -0.45 eÅ^{-3}. Computations were carried out as for **1**.

Characterization

Raman spectra were measured on pure solids on a Perkin–Elmer 1700X Fourier-Transform spectrometer with a Spectron Laser Systems Nd/YAG laser (excitation at 1064 nm) and, for [Cu(napy)$_2$Cl$_2$] only, as a spinning disc on a potassium bromide base using a Spex Ramalog V instrument and Spex Datamate data acquisition unit with a Coherent Innova 70 argon-ion laser (excitation at 514.5 nm). Carbon, nitrogen and hydrogen anlayses were carried out by the Microanalytical Department, Imperial College.

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