Complexes of 5,7-Dimethyl-1,8-naphthyridine-2-ol(dimenol): EPR Spectra of an Unusual Copper(II) Dimer containing Dimenol and Acetate Bridges, and Crystal Structure of $[Rh(O_2CC_3H_7)_2(dimenol)]_2$

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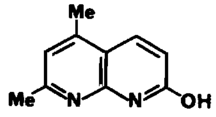
Abstract

The preparations are reported of complexes of 5,7-dimethyl-1,8-naphthyridine-2-ol (= dimenol) with metal ions of the series Mn–Zn. Reaction of dimenol with copper(II) acetate yields a dark blue complex of stoichiometry $Cu(dimenol)(CH_3CO_2)$ which, from its X- and Q-band EPR spectra, is dimeric containing antiferromagnetically coupled pairs of Cu(II) ions. Analogous reactions with rhodium(II) acetate and butyrate gave the adducts $[Rh(O_2CR)_2(dimenol)]_2$. The intense violet butyrate $[Rh(O_2CC_3H_7)_2(dimenol)]_2$ crystallizes in the space group $P2_1/n$ with $a = 11.474(2)$, $b = 10.247(1)$, $c = 17.129(3)$ Å, $\beta = 101.67(1)°$, and $Z = 2$. It has the standard dinuclear rhodium(II) carboxylate lantern structure with Rh–Rh = 2.409(1) Å. The dimenol ligands coordinate in axial positions *via* N(8) of the naphthyridine. The Rh–N distance (2.387(4) Å) is one of the longest yet reported. Attention is drawn to a potential danger in using colour as an indicator of coordination mode of an ambidentate ligand L in $[Rh(O_2CR)_2L]_2$ complexes.

Introduction

There is continuing interest [1] in the complexes formed by 1,8-naphthyridine and its derivatives, as these ligands show diverse coordination behaviour. During studies [2] of the coordinating abilities of exocyclic oxygen or sulphur atoms in purines, pyrimidines, and related heterocycles we observed the formation of a platinum 'blue' by 5,7-dimethyl-1,8-naphthyridine-2-ol (**I**, dimenol). Although we were unable satisfactorily to characterize the nature of this dimenol/Pt blue, our ancillary investigations into the coordination chemistry of **I** yielded an interesting mixed bridge copper(II) dimer, $[Cu(dimenol)(CH_3CO_2)]_2$. In view of recent reports of mixed bridged complexes of rhodium(I) [1] and rhodium(II) [3] with naphthyridine derivatives, we are prompted to describe the synthesis and EPR spectra of the copper complex, the isolation of some other complexes of **I**, and the results of an X-ray diffraction study of the structure of $[Rh(C_3H_7CO_2)_2(dimenol)]_2$.



I

Results and Discussion

The metal complexes of dimenol we have prepared are listed in Table I. For the metal ions studied, the most common product stoichiometry, under the reaction conditions employed, was 4:1, a stoichiometry well established for 1,8-naphthyridine as a ligand [4]. The steric influence of the methyl group in the 7-position would be expected to lead to asymmetry in the extent to which N(1) and N(8) respectively coordinate, and hence to distorted ligand fields. This is clearly indicated by the EPR spectrum of $Mn(dimenol)_4(ClO_4)_2 \cdot H_2O$ (Fig. 1), which shows pronounced zero-field splitting. The form of this spectrum suggests that dimenol is not binding in a simple monodentate fashion to produce a distorted tetrahedral coordination geometry [5].

The EPR spectrum of $Cu(dimenol)_4(ClO_4)_2$ (Fig. 2) is typical of copper(II) in a square or a *trans*-distorted octahedral environment and its electronic spectrum (15,800 cm^{-1}) is in agreement with this. Both the electronic spectrum and the EPR spectrum of the corresponding nitrate, $Cu(dimenol)_4(NO_3)_2$ differ from those of the perchlorate. For the nitrate the main d–d band is at

0020-1693/85/$3.30

TABLE I. Analytical Data of Some Complexes of 5,7-Dimethyl-1,8-naphthyridine-2-ol (=L).

Complex	M:L ratio used in synthesis	Colour	Analysis (%)					
			Found			Calc.		
			C	H	N	C	H	N
$MnL_4Cl_2 \cdot H_2O$	1:2	Yellow	57.50	5.30	12.71	57.15	5.04	13.33
$MnL_4(ClO_4)_2 \cdot H_2O$	1:2	Yellow	49.70	4.23	11.38	49.57	4.37	11.58
$FeL_4(ClO_4)_2$	1:2	Yellow	50.18	4.27	11.35	50.46	4.24	11.78
FeL_2Cl_3	1:2	Red	46.72	3.99	10.55	47.04	3.95	10.97
$CoL_3Cl_2 \cdot 2H_2O$	1:3	Blue	52.65	5.09	12.39	52.34	4.98	12.21
$CoL_3(NO_3)_2$	1:3	Pink	50.72	4.16	15.14	51.07	4.29	15.88
$CoL_4(ClO_4)_2$	1:2	Pink	50.43	4.19	11.70	50.33	4.22	11.74
NiL_3Cl_2	1:3	Yellow	55.41	4.92	12.75	55.25	4.64	12.89
NiL_4Br_2	1:3	Yellow	51.89	4.61	12.07	52.44	4.40	12.24
$NiL_4(ClO_4)_2$	1:2	Yellow	50.45	4.13	11.68	50.34	4.22	11.74
$CuL(CH_3CO_2)$	1:1	Dark blue	48.54	4.00	9.40	48.75	4.09	9.48
CuL_2Cl_2	1:2	Purple	49.62	4.13	11.49	49.75	4.18	11.60
$CuL_4(NO_3)_2$	1:2	Yellow	54.29	4.52	15.64	54.33	4.55	15.84
$CuL_4(ClO_4)_2$	1:2	Yellow	49.91	4.12	11.61	50.05	4.20	11.68
$ZnL_4(ClO_4)_2$	1:2	White	49.99	4.21	11.58	49.97	4.50	11.66
$CdL_4(ClO_4)_2$	1:2	White	47.84	4.04	11.06	47.63	4.00	11.04
$CdLCl_2$	1:2	White	33.61	2.74	7.68	33.58	2.82	7.84
$RhL(CH_3CO_2)_2$	1:1	Steel blue	41.96	4.00	6.90	42.55	4.08	7.09
$RhL(C_3H_7CO_2)_2$	1:1	Intense violet	47.90	5.28	6.12	47.90	5.36	6.21

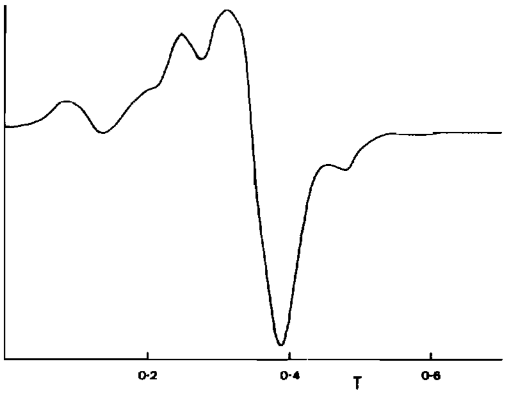


Fig. 1. X-Band EPR spectrum of $Mn(dimenol)_4(ClO_4)_2 \cdot H_2O$.

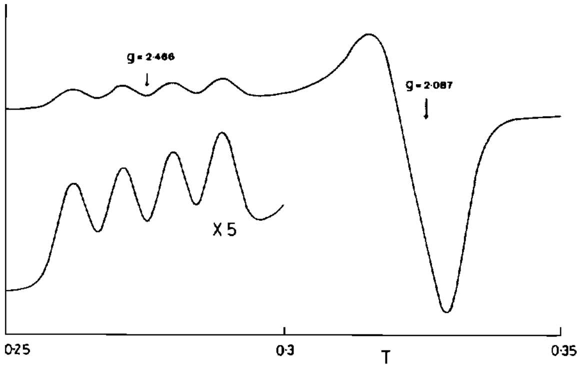


Fig. 2. X-Band EPR spectrum of $Cu(dimenol)_4(ClO_4)_2$.

lower energy (13,300 cm^{-1}) and the EPR spectrum (Fig. 3) suggests a pronounced rhombic environment for the copper(II) ion. The IR spectrum was consistent with the presence of ionic nitrate.

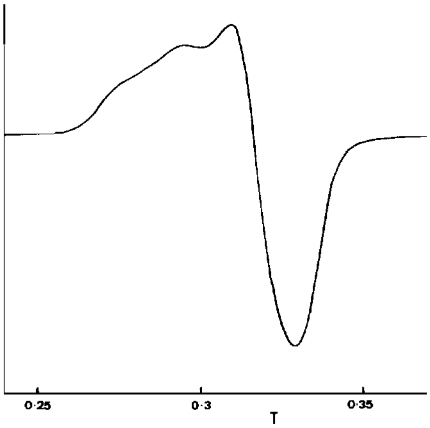


Fig. 3. X-Band (9.513 GHz) EPR spectrum of $Cu(dimenol)_4(NO_3)_2$.

The 3:1 complexes $Co(dimenol)_3(NO_3)_2$ and $Ni(dimenol)_3Cl_2$ have low intensity electronic bands in the visible region indicative of six-coordination, as reported [6] for 3:1 complexes with 2,7-dimethyl-1,8-naphthyridine. One exception is the blue complex $Co(dimenol)_3Cl_2 \cdot 2H_2O$ which was a 1:1 electrolyte in nitromethane (Λ_m 74 ohm^{-1}) and had an intense electronic band at 15,400 cm^{-1} suggesting distorted tetrahedral coordination.

When copper(II) chloride was reacted with I a purple complex of stoichiometry Cu(dimenol)$_2$Cl$_2$ was obtained. Its EPR spectrum (Fig. 4) was typical of monomeric Cu(II) in a rhombic environment. The IR spectrum had only one ν(Cu–Cl) band (at 300 cm^{-1}) suggesting a *trans*-arrangement and a structure similar to that reported [7] for Cu(2,7-dimethyl-1,8-naphthyridine)$_2$Cl$_2$.

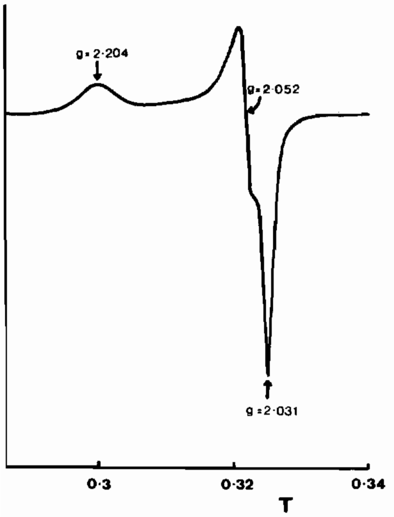


Fig. 4. X-Band EPR spectrum of Cu(dimenol)$_2$Cl$_2$.

Reaction of copper(II) acetate and I in hot ethanol resulted in deprotonation of I and the formation of a very dark blue solid of stoichiometry Cu(C$_{10}$H$_9$N$_2$O)(CH$_3$CO$_2$). This product was obtained irrespective of whether 2:1 or 1:1 ratios of dimenol: copper were used.

The low magnetic moment of the complex (1.42 BM at room temperature) indicates the presence of antiferromagnetically coupled copper(II) ions. Attempts to obtain suitable crystals for X-ray diffraction studies were unsuccessful, but the EPR spectra of the compound at X-band, *ca.* 9.5 GHz (Fig. 5), and at Q-band, *ca.* 36 GHz (Fig. 6), show clearly that the complex is dinuclear, as they are typical of S = 1 species.

The spectral components are better resolved at Q-band frequency, and the assignments shown in Fig. 6 yield the following parameters: g_z 2.27, g_{xy} 2.03, D = 0.23 cm^{-1} (there was no significant splitting of the bands B_{xy1} or B_{xy2} so the parameter E, representing the rhombic component [8], is zero or, at least, very small). These values may be compared with those for copper(II) acetate monohydrate (g_z 2.35, g_{xy} 2.08, D = 0.34 cm^{-1}) and similar values for related four-carboxylate bridged copper(II) dimers [9], and those for complexes such as Cu(4-azabenzimidazole)$_2$Cl$_2$·2H$_2$O (g_z 2.29, g_{xy} 2.05, D = 0.134 cm^{-1}) [10] which contain four bridging N-donor heterocycle groups.

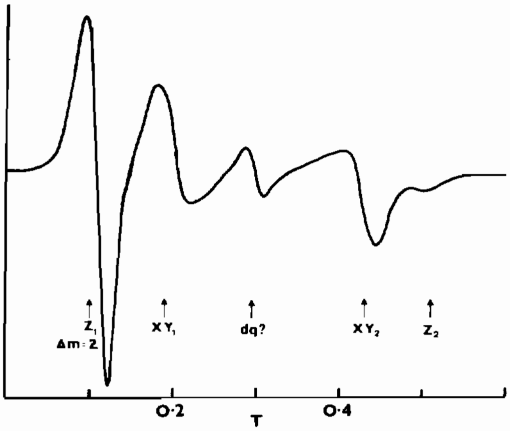


Fig. 5. X-Band EPR spectrum of [Cu(dimenol)(CH$_3$CO$_2$)]$_2$.

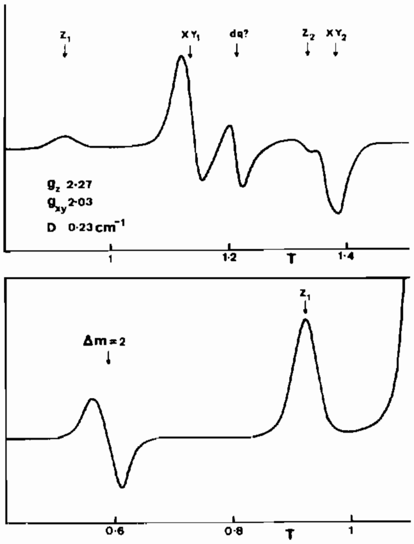
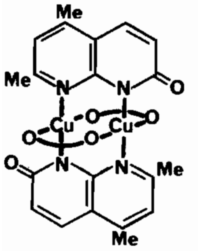


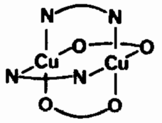
Fig. 6. Q-Band EPR spectrum of [Cu(dimenol)(CH$_3$CO$_2$)]$_2$. (Note: lower section of diagram is at higher instrument gain to enhance the weak $\Delta m = 2$ band; the Z_1 band provides a common reference for both sections of the diagram).

The assignment of the band at 0.3 T in the X-band spectrum of [Cu(dimenol)(CH$_3$CO$_2$)]$_2$, and the corresponding band at 1.22 T in the Q-band spectrum, as the double quantum transition must be regarded as very tentative. Although such a band might be expected at those respective fields, the absorptions could also be due to small amounts of monomeric, S = 1/2, copper(II) species which are well known to accompany the S = 1 spectra of copper(II) dimers.

Several structures are possible for [Cu(dimenol)(CH$_3$CO$_2$)]$_2$. On steric grounds, it seems likely that the dimenol ligands will adopt a *trans*-arrangement with respect to the relative dispositions of the methyl groups in the 7-position, as in **II**. Each pair of dimenol ligands could then be either *trans*-about the Cu–Cu axis, as in **II**, or *cis*-, as in **III**.



II



III

Unfortunately the very small, or zero, value of E obtained from the EPR data does not permit a decision to be made between these geometries, as the zero-field splitting tensor axes may not lie along the Cu-donor atom molecular axes. A *trans*-arrangement of naphthyridines (napy) has been found [11] in $[Cu(napy)Cl_2]_2$, but *cis*-arrangements have been proposed for substituted naphthyridine bridges in complexes of rhodium(I) [1] and rhodium(II) [3].

An analogous reaction using rhodium(II) acetate or butyrate in place of copper(II) acetate did not result in replacement of the carboxylate bridges by dimenol but gave the adducts $Rh(O_2CR)_2$(dimenol), where $R = CH_3$ or C_3H_7 respectively. This observation is in line with the fact that more forcing conditions are generally required to substitute the bridges in rhodium(II) carboxylate dimers, than in their more labile Cu(II) analogues.

The question then arises as to whether the terminal dimenol ligands are bonded to rhodium by the exocyclic oxygen atom or by one of the ring nitrogens, and, if the latter, by which one. The colours of the rhodium(II) carboxylate dimers have frequently been used as a guide [12–14] to the nature of the donor atoms bonded in the terminal positions. Many such complexes involving N-donor atoms are pink or red, and those with O-donors are generally green or blue-green [13], but exceptions to this classification by colour are known. Crystals of $[Rh(O_2CC_2H_5)(acridine)]_2$ are reported [15] to be dichroic (green/dark red depending on orientation), and in this compound the acridine molecules coordinate in terminal positions but with exceptionally long Rh–N bonds (2.413 Å). The analogous acetate $[Rh(O_2CCH_3)_2(acridine)]_2$ is green [16]. Variation of the alkyl group of the carboxylate with constant terminal ligand L in $[Rh(O_2CR)_2L]_2$ has virtually no effect on colour, at least for R groups of the type C_nH_{2n+1} [16].

The colours of the $Rh(O_2CR)_2$(dimenol) complexes we have obtained are dark steel blue ($R = CH_3$) and intense violet ($R = C_3H_7$) respectively. These colours would be compatible with dimenol coordination *via* the exocyclic oxygen or *via* the stronger donor, but more sterically constrained, ring nitrogen atoms. The butyrate could be isolated as single crystals of suitable quality for an X-ray diffraction study. This has shown the molecular geometry of that complex to be as in Fig. 7. Each molecule is dinuclear with the two rhodium atoms bridged by four butyrate groups. Each rhodium is also coordinated to the nitrogen, N(8), of the 5,7-dimethyl-substituted ring of the naphthyridine ligand. There is a crystallographic centre of symmetry at the centre of the Rh–Rh bond.

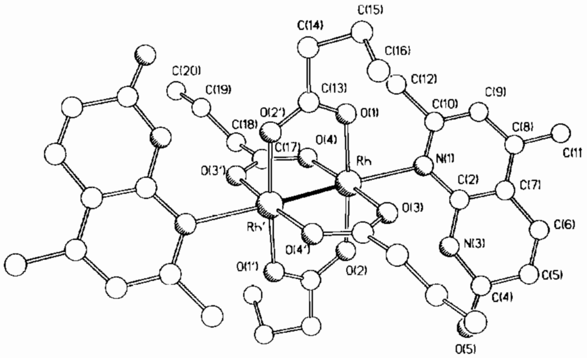


Fig. 7. Molecular structure of $[Rh(O_2CC_3H_7)_2(dimenol)]_2$, giving the crystallographic numbering scheme.

The axial N–Rh–Rh′–N′ chain is very nearly linear with NRhRh angles of 177.4(1)°. The two groups of four equatorial oxygen atoms are nearly perfectly eclipsed with respect to each other with a maximum ORhRhO torsion angle of 1°. The ring atoms of the naphthyridine moiety are coplanar with a maximum deviation from the least-squares plane of 0.03 Å (for C(4)); O(5) lies 0.08 Å from this plane. The plane of the naphthyridine ligand bisects the O(1)RhO(4) and O(2)RhO(3) angles causing a small splaying of these angles (91.8(1) and 90.7(1)° respectively) and a corresponding contraction of those for O(1)RhO(3) and O(2)RhO(4) (88.7(1) and 88.5(1)° respectively).

The four independent Rh–O bonds do not differ significantly from each other and have an average length of 2.036 Å. The Rh–Rh distance (2.409(1) Å) is similar to that observed in other bridged systems [14]. The Rh–N distances (2.387(4) Å) are, however, very long. There is, we believe, only one reported example of a longer Rh–N bond in an analogous system, in $[Rh(O_2CC_2H_5)_2(acridine)]_2$, referred to above, in which Rh–N = 2.413(3) Å [15]. There the Rh–Rh distance (2.417(1) Å) was also slightly longer.

The structure is stabilised by a strong intramolecular N–H···O hydrogen bond (2.84 Å, $\widehat{NHO}$ = 147°) between the other potential ligating nitrogen atom, N(3), of the naphthyridine ligand and the butyrate oxygen O(3) (Fig. 7). The distance of N(3) to the adjacent butyrate oxygen atom, O(2), is 3.01 Å.

The packing of the molecules is normal van der Waals. There is no close parallel stacking of the naphthyridine ligands.

Because of the apparent influence of the length of the Rh–N bonds on the colours of these compounds and some others with relatively long Rh–N axial bonds we have measured the electronic spectra of $[Rh(O_2CR)_2(dimenol)]_2$ ($R = CH_3$, C_3H_7). Their poor solubility restricted measurements to the solid phase by the reflectance method.

It is well established [14] that it is the lowest energy band (usually termed band I), of the four main UV–Vis bands observed for the dinuclear rhodium(II) carboxylate adducts, whose position is most sensitive to changes in the axial ligand. The wavelengths at which we observe band I in the reflectance spectra of $[Rh(O_2CR)_2(dimenol)]_2$ are listed in Table II and compared with results for other solid complexes reported in the literature [14]. It appears that the established trend in band I position, and hence colour, with change in identity of donor atom in the axial position, extends to a sensitivity of the band to the Rh–donor atom bond length for ligands containing similar donor atoms.

Our observations on the dimenol complexes, taken together with information available in the literature, emphasize the dangers in ascribing the coordination mode of an ambidentate ligand in the axial position in the rhodium(II) carboxylates simply on the basis of colour and/or electronic spectra, without considering steric, or other, factors which may cause 'anomalous' Rh–donor atom bond lengths.

Experimental

Preparation

The complexes were prepared by the following general method. An ethanolic solution of the appropriate metal salt was added to one of the ligand in hot ethanol, in the stoichiometric ratios given in Table I. The mixture was refluxed with stirring, and in most cases the complexes separated out. They were filtered off, washed with hot ethanol and dried *in vacuo*. Some additional details for individual compounds are given below (L = dimenol) $MnL_4Cl_2 \cdot H_2O$: reaction solution refluxed for 5 days. Concentration of the solution gave a pale yellow precipitate. Magnetic moment 5.94 B.M. FeL_2Cl_3: a red solid separated during 3 days refluxing of the reactants. Magnetic moment 5.85 B.M. $CoL_3Cl_2 \cdot 2H_2O$: blue solid obtained on concentrating the reaction mixture after 5 days reflux. Magnetic moment 4.80 B.M. CuL_2Cl_2: reaction mixture refluxed for a week then concentrated by boiling. Rapid addition of cold ethanol to the hot concentrated solution gave a purple precipitate. Λ_m in nitromethane 18 $ohm^{-1}\,cm^2\,mol^{-1}$.

Microanalyses (Table I) were by the Microanalytical Laboratory, Imperial College, the Galbraith Microanalytical Laboratory, and the Chemical Laboratory of the Department of Fossil Fuels, Guernavaca, Morelos.

Physical Measurements

Electronic spectra were measured by the diffuse reflectance technique using Cary 14 and Beckman DK2 spectrometers. A Perkin-Elmer Model 681 spectrometer was used to obtain IR spectra in the 600–4000 cm^{-1} region. Spectra below 600 cm^{-1} were obtained by courtesy of the Institute of Materials Research, UNAM. Magnetic measurements were made by the Gouy method.

EPR spectra were measured at room temperature using polycrystalline samples. X-Band measurements were made on a Varian E-12 spectrometer. The Q-band spectrometer comprised a Varian 36 GHz microwave bridge and a Newport 12 inch type-F magnet powered by a C905 rotary generator and post stabilizer.

TABLE II. Comparison of Colours, Band I Positions from Solid State Spectra, and Rh–L (Axial) Bond Lengths for $[Rh(O_2CR)_2(dimenol)]_2$ ($R = CH_3$, C_3H_7) with those of other Rhodium(II) Carboxylates. [Comparison Data from Ref. 14].

Compound	Colour	Band I (nm)	Rh–L (Å)
$[Rh(O_2CCH_3)_2(dimenol)]_2$	Steel blue	574	^{a}
$[Rh(O_2CC_3H_7)_2(dimenol)]_2$	Intense violet	578	2.398
$[Rh(O_2CCH_3)_2py]_2$	Red	514	2.227
$[Rh(O_2CCH_3)_2(NHEt_2]_2$	Red	530	2.301
$[Rh(O_2CCH_3)_2(caffeine)]_2$	Violet	^{b}	2.315
$[Rh(O_2CC_2H_5)_2(acridine)]_2$	Green/Red^{c}	^{b}	2.413
$[Rh(O_2CCH_3)_2(OH_2)]_2$	Green	580	2.310
$[Rh(O_2CCH_3)_2]_2$	Green	617	–

^{a}Unknown. ^{b}Not reported. ^{c}Dichroic crystals; colour of powder not reported.

X-Ray Study

[Rh($O_2CC_3H_7$)$_2$(dimenol)]$_2$ crystallises as intense violet, platey needles elongated along *c*. The crystal data are: $C_{36}H_{48}N_4O_{10}Rh_2$, monoclinic, $a = 11.474(2)$, $b = 10.247(1)$, $c = 17.129(3)$ Å, $\beta = 101.67(1)°$, $V = 1972$ Å^3, space group $P2_1/n$, $Z = 2$, mol. wt. 902.6, $D_c = 1.53$ gm^{-3}, μCu-K$_\alpha$ = 73 cm^{-1}. Refined unit cell parameters were obtained by centering 16 reflections on a Nicolet R3m diffractometer. 1780 independent observed reflections [$\theta \leqslant 50°$, $|F_o| > 3\sigma(|F_o|)$] were measured with Cu-K$_\alpha$ radiation (graphite monochromator) using ω-scans. The data were corrected for Lorentz and polarisation factors and a numerical absorption correction was applied.

The structure was solved by the heavy-atom method and the non-hydrogen atoms refined anisotropically. The orientations of the methyl groups' hydrogen atoms were determined from a ΔF map and the groups refined as rigid bodies. The remaining hydrogens were placed at idealised positions (C–H = 0.96 Å), assigned isotropic thermal parameters, $U(\text{H}) = 1.2\ U_{eq}(\text{C})$, and allowed to ride on their parent carbon atoms. Refinement was by block-cascade full matrix least-squares to $R = 0.032$, $R_w = 0.031$, [$w^{-1} = \sigma^2(F) + 0.00013\ F^2$]. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system [17]. Atomic scattering facors were from reference [18].

The fractional atomic coordinates of the non-hydrogen atoms are listed in Table III. Table IV lists the bond lengths and valence angles.

TABLE III. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3).

Atom	*x*	*y*	*z*	*U*^{a}
Rh	4715(1)	558(1)	551(1)	31(1)
O(1)	6484(3)	820(4)	1009(2)	42(1)
O(2)	2987(3)	234(3)	14(2)	40(1)
O(3)	4728(3)	2243(3)	−70(2)	44(1)
O(4)	4719(3)	−1211(3)	1094(2)	44(1)
N(1)	4108(4)	1739(4)	1602(2)	31(1)
C(2)	3238(4)	2650(5)	1437(3)	30(2)
N(3)	2591(4)	2700(4)	667(2)	39(2)
C(4)	1681(5)	3547(6)	387(3)	45(2)
O(5)	1151(4)	3476(4)	−314(2)	63(2)
C(5)	1423(5)	4469(6)	960(3)	46(2)
C(6)	2010(5)	4441(6)	1710(3)	48(2)
C(7)	2949(4)	3523(5)	1990(3)	34(2)
C(8)	3566(5)	3439(5)	2784(3)	40(2)
C(9)	4444(4)	2513(5)	2954(3)	37(2)
C(10)	4711(4)	1687(5)	2371(3)	33(2)
C(11)	3287(6)	4325(7)	3422(4)	67(3)
C(12)	5663(5)	694(6)	2592(3)	52(2)
C(13)	7248(5)	375(5)	647(3)	39(2)
C(14)	8537(5)	608(6)	997(4)	58(2)
C(15)	8792(6)	2025(7)	1237(4)	81(3)
C(16)	8459(8)	2943(8)	535(5)	102(4)
C(17)	4998(5)	−2223(6)	750(3)	46(2)
C(18)	4980(7)	−3514(6)	1155(4)	76(3)
C(19)	6046(8)	−4257(8)	1254(6)	118(4)
C(20)	6114(7)	−5531(6)	1644(4)	77(3)

^{a}Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE IV. Bond Lengths and Angles.

Bond lengths (Å)	
Rh–O(1)	2.041(3)
Rh–O(3)	2.030(3)
Rh–N(1)	2.387(4)
O(1)–C(13)	1.256(7)
O(3)–C(17′)	1.266(7)
N(1)–C(2)	1.354(6)
C(2)–N(3)	1.376(6)
N(3)–C(4)	1.368(7)
C(4)–C(5)	1.436(8)
C(6)–C(7)	1.438(7)
C(8)–C(9)	1.372(7)
C(9)–C(10)	1.389(7)
C(13)–C(14)	1.498(7)
C(14)–C(15)	1.522(9)
C(17)–C(18)	1.496(9)
C(18)–C(19)	1.421(11)
Rh–O(2)	2.036(3)
Rh–O(4)	2.037(3)
Rh–Rh′	2.409(1)
O(2)–C(13′)	1.274(7)
O(4)–C(17)	1.265(7)
N(1)–C(10)	1.360(6)
C(2)–C(7)	1.391(7)
C(4)–O(5)	1.233(6)
C(5)–C(6)	1.324(7)
C(7)–C(8)	1.402(6)
C(8)–C(11)	1.504(9)
C(10)–C(12)	1.484(8)
C(13)–O(2′)	1.274(7)
C(15)–C(16)	1.514(10)
C(17)–O(3′)	1.266(7)
C(19)–C(20)	1.461(11)
Bond angles (deg.)	
O(1)–Rh–O(2)	175.3(2)
O(2)–Rh–O(3)	90.7(1)
O(2)–Rh–O(4)	88.5(1)
O(1)–Rh–N(1)	93.6(1)
O(3)–Rh–N(1)	89.9(1)
O(1)–Rh–Rh′	87.5(1)
O(3)–Rh–Rh′	87.7(1)
N(1)–Rh–Rh′	177.4(1)

(continued on facing page)

TABLE IV *(continued)*

Rh–O(2)–C(13′)	119.5(3)
Rh–O(4)–C(17)	119.6(4)
Rh–N(1)–C(10)	122.8(3)
N(1)–C(2)–N(3)	117.3(4)
N(3)–C(2)–C(7)	118.2(4)
N(3)–C(4)–O(5)	119.7(5)
O(5)–C(4)–C(5)	125.1(5)
C(5)–C(6)–C(7)	122.6(5)
C(2)–C(7)–C(8)	118.6(5)
C(7)–C(8)–C(9)	117.0(5)
C(9)–C(8)–C(11)	121.2(5)
N(1)–C(10)–C(9)	121.9(4)
C(9)–C(10)–C(12)	119.5(4)
O(1)–C(13)–O(2′)	125.0(5)
C(13)–C(14)–C(15)	112.4(5)
O(4)–C(17)–C(18)	118.7(5)
C(18)–C(17)–O(3′)	116.2(5)
C(18)–C(19)–C(20)	119.9(8)
O(1)–Rh–O(3)	88.7(1)
O(1)–Rh–O(4)	91.8(1)
O(3)–Rh–O(4)	175.4(1)
O(2)–Rh–N(1)	91.0(1)
O(4)–Rh–N(1)	94.7(1)
O(2)–Rh–Rh′	87.9(1)
O(4)–Rh–Rh′	87.7(1)
Rh–O(1)–C(13)	120.1(3)
Rh–O(3)–C(17′)	119.9(3)
Rh–N(1)–C(2)	120.4(3)
C(2)–N(1)–C(10)	116.1(4)
N(1)–C(2)–C(7)	124.6(4)
C(2)–N(3)–C(4)	125.8(4)
N(3)–C(4)–C(5)	115.2(4)
C(4)–C(5)–C(6)	120.9(5)
C(2)–C(7)–C(6)	117.3(4)
C(6)–C(7)–C(8)	124.1(5)
C(7)–C(8)–C(11)	121.9(5)
C(8)–C(9)–C(10)	121.9(4)
N(1)–C(10)–C(12)	118.5(5)
O(1)–C(13)–C(14)	118.4(5)
C(14)–C(13)–O(2′)	116.6(5)
C(14)–C(15)–C(16)	112.0(6)
O(4)–C(17)–O(3′)	125.1(5)
C(17)–C(18)–C(19)	115.9(7)

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