Dimolybdenum(II) and diruthenium(II) complexes with 2-substituted 7-methyl-1,8-naphthyridines as bridging ligands

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Abstract

The dimolybdenum(II) complexes [Mo$_2$(monp)$_4$] (**1**) and [Mo$_2$(msnp)$_4$] (**2**) (Hmonp = 7-methyl-1,8-naphthyridin-2-one, Hmsnp = 7-methyl-1,8-naphthyridin-2-thione) were prepared by reaction of Mo(CO)$_6$ with the appropriate ligand in diglyme at 190 °C and their structures established by X-ray structural analysis. Four monoanionic ligands bridge the quadrupole Mo–Mo bonds in **1** and **2** and display respectively $1\kappa^1 N{:}2\kappa^1 O$ and $1\kappa^1 N{:}2\kappa^1 S$ coordination modes. *trans*-MoX$_2$Y$_2$ geometries are observed for the individual molybdenum atoms leading to steric crowding of the mutually *trans*-sited ligands in **2**, which is alleviated by a twisting distortion of these ligands with an average torsion angle of 8.0°. Respective Mo–Mo distances of 2.090(4) and 2.131(2) are observed in **1** and **2**. The solid-state reaction of Ru$_2$(OAc)$_4$Cl with Hmonp at 190 °C leads to the formation of [Ru$_2$(monp)$_4$] in which the *trans*-sited ligands display a $1\kappa^1 N{:}2\kappa^1 N'$ coordination pattern. An average twist of 17.7° from the eclipsed conformation is observed which reduces steric repulsions between neighbouring substituents of mutually *cis* monoanionic ligands. The Ru–Ru bond length of 2.258(2) Å and the magnetic moment of 2.51 BM at 293 K are in accordance with a $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*2}$ electronic configuration.

Key words: Crystal structures; Molybdenum complexes; Ruthenium complexes; Bidentate ligand complexes; Dinuclear complexes

Introduction

1,8-Naphthyridine (np) and its derivatives have often been proposed as potential dinucleating ligands capable of bridging metal–metal bonds or holding two metal atoms in close proximity [1]. However, np has generally been observed to function as a mono- or bidentate ligand towards a single metal atom in mononuclear complexes such as [Cu(np)$_2$Cl$_2$] [2a], [Pt(np)(PEt$_3$)$_2$Cl]BF$_4$ [2b], [Cd(np)$_4$](ClO$_4$)$_2$ [2c] or [Fe(np)$_4$](ClO$_4$)$_2$ [2d]. Examples of dinuclear complexes containing bridging np ligands are provided by the respective copper(I) and copper(II) complexes [Cu$_2$(np)$_2$](ClO$_4$)$_2$ [3a] and [Cu$_2$(np)$_2$Cl$_4$] [3b], the silver(I) complex [Ag$_2$(np)$_2$](ClO$_4$)$_2$ [3a] and the mixed-valence nickel complex [Ni$_2$(np)$_4$Br$_2$]BPh$_4$ [3c], all of which were characterised by X-ray structural analysis. The dirhodium(II) complex [Rh$_2$(np)$_4$]Cl$_4$ was prepared by Kaska and co-workers [4a] by the reaction of [Rh$_2$(OAc)$_4$] with np in methanol in the presence of an equivalent of 1 M HCl. A series of dinuclear compounds [Rh$_2$(OAc)$_3$L]PF$_6$ has also been reported, which contain crescent-shaped ligands L such as dpnp (2,7-bis(2-pyridyl)-1,8-na-phthyridine) with a central 2,7-substituted np fragment [4a–d]. The ligand dpnp was also recently employed in the synthesis of [Ru$_2$Cl$_2$(bpy)$_2$(μ-dpnp)](PF$_6$)$_2$ and [Ru$_2$(OAc)$_3$(μ-dpnp)]PF$_6$, both of which contain the Ru$_2$$^{4+}$ core and axially coordinating dpnp pyridine rings [5a]. Both the latter complex and the structurally analogous Ru$_2$$^{5+}$ species [Ru$_2$(OAc)$_3$(μ-dcnp)] (dcnp = 1,8-naphthyridine-2,7-dicarboxylate) [5b] were structurally characterised by X-ray crystallography. A tetranuclear complex [{Mo$_2$(O$_2$C-t-Bu)$_3$}$_2$ (μ-donp)]·2thf (H$_2$donp = 1,8-naphthyridine-2,7-dione) has been studied by Chisholm and co-workers [6a, b] as a molecular model for subunits of stiff-chain polymers. The Mo–Mo distances in the Mo$_4$ chain alternate as 2.10 (terminal), 3.17 (central) and 2.10 (terminal) Å and correspond formally to two discrete Mo–Mo quadrupole bonds in close proximity.

The ligand properties of 1,8-naphthyridin-2-one (Honp) and 5,7-dimethyl-1,8-napththyridin-2-one (Hdmonp) have also been investigated. Oro and co-workers reported a series of di- and trinuclear-(diene)rhodium(I) complexes (diene = norbornadiene, 1,5-cyclooctadiene) in which two or three rhodium

atoms are held close to one another [7a–c], e.g. $d(Rh-Rh) = 2.880(2)$ Å in $[Rh_2(\mu\text{-onp})_2(CO)_4]$ [7a]. A dinuclear copper(II) species $[Cu(OAc)(dmonp)]_2$ was prepared by Goodgame and co-workers [8] by the reaction of copper(II) acetate with Hdmonp in hot ethanol. In contrast, the analogous reaction with $[Rh_2(OAc)_4]$ did not result in replacement of the carboxylate bridges, but yielded simply an axial adduct $[Rh_2(OAc)_4(Hdmonp)_2]$, in which the Hdmonp ligands coordinate through their N1 nitrogens.

No dimolybdenum(II) or diruthenium(II) complexes of the type M_2L_4 have, to our knowledge, been reported for 1,8-naphthyridine ligands L. 7-Methyl-1,8-naphthyridin-2-one (Hmonp) and 7-methyl-1,8-naphthyridin-2-thione (Hmsnp) are ambidentate ligands which can potentially bridge two metal atoms via $1\kappa^1N:2\kappa^1O(S)$ or $1\kappa^1N:2\kappa^1N'$ coordination modes. In this work we describe the synthesis and X-ray structural characterisation of the complexes $[Mo_2(monp)_4]$ (1), $[Mo_2(msnp)_4]$ (2) and $[Ru_2(monp)_4]$ (3).

Experimental

All solvents were dried and distilled before use. Electronic spectra were recorded on a Perkin-Elmer Lambda 15, IR spectra (KBr discs) on Perkin-Elmer 1700 and 1760 spectrometers. FAB-MS were measured on a Fisons VG Autospec, ^1H NMR spectra on a Bruker AM 400 with δ values registered as ppm relative to the signal of the deuterated solvent. Elemental analyses were performed on a Carlo Erba 1106. The 1,8-naphthyridine derivative Hmonp and $[Ru_2(OAc)_4Cl]$ were synthesised according to literature procedures [9, 10].

Preparation of Hmsnp and complexes 1–3

2-Mercapto-7-methyl-1,8-naphthyridine (Hmsnp)

2-Chloro-7-methyl-1,8-naphthyridine (Hmcnp) was prepared from the 2-hydroxy derivative by the method of Brown [9a]. The reaction of Hmcnp to Hmsnp was performed in analogy to the literature preparation of 2-mercapto-1,8-napththyridine [9b]. 10 g (56.0 mmol) Hmcnp and 4.6 g (60.4 mmol) thiourea were heated for 3 h in refluxing methanol under an argon atmosphere. The reaction mixture was then cooled and neutralised with KOH. After extraction of the product with chloroform, the solvent was removed to yield Hmsnp as a brown solid (yield 91%). *Anal.* Found: C, 62.2; H, 4.6; N, 16.7. Calc. for $C_9H_8N_2S$ ($M = 176.2$): C, 61.3; H, 4.6;
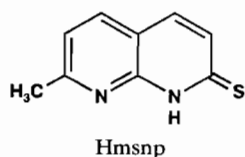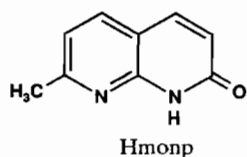
N, 15.9%. ^1H NMR (CDCl$_3$), 2.70 (s, 3H, CH$_3$), 7.1 (d, 1H, H3), 7.4 (d, 1H, H6), 7.8 (d, 1H, H4), 8.05 (d, 1H, H5) ppm. IR: 1608s, 1491s, 1433m, 1309w, 1229m, 1138s, 1101s, 847m, 804m, 798m cm^{-1}.

$[Mo_2(monp)_4]$ (1)

0.133 g (0.5 mmol) Mo(CO)$_6$ was heated for 2.5 h in 25 ml diglyme under argon at 190 °C together with 0.160 g (1.0 mmol) Hmonp. The solvent was removed and the product dissolved in 25 ml refluxing toluene. After filtration 1 was obtained as a red microcrystalline product by slow gas diffusion of pentane into the solution (yield 81%). Crystals of 1 suitable for an X-ray structural analysis were grown by diffusion of diethyl ether into a chlorobenzene solution of 1. *Anal.* Found: C, 51.6; H, 4.2; N, 12.7. Calc. for $C_{36}H_{28}N_8O_4Mo_2$ ($M = 828.6$): C, 52.2; H, 3.4; N, 13.5%. FAB-MS: m/z (%) 829 (100) $[M^+]$, 669 (16) $[M^+ - \text{monp}]$. ^1H NMR (CDCl$_3$), 2.59 (s, 3H, CH$_3$), 6.6 (d, 1H, H3), 7.0 (d, 1H, H6), 7.62 (d, 1H, H4), 7.74 (d, 1H, H5) ppm. IR: 1631m, 1600s, 1559m, 1508s, 1454s, 1382s, 1261w, 1218w, 1137m, 1097w, 1027w, 838m, 739m, 600w cm^{-1}. UV–Vis (CH$_2$Cl$_2$): λ_{max} (ϵ (1 mol^{-1} cm^{-1})), 503 (801), 323 (2183), 283 (1633) nm.

$[Mo_2(msnp)_4]$ (2)

0.134 g (0.5 mmol) Mo(CO)$_6$ was heated together with 0.177 g (1.0 mmol) Hmsnp for 2 h in 25 ml diglyme at 190 °C under argon. The solvent was removed and the product dissolved in 20 ml CH$_2$Cl$_2$. After filtration the CH$_2$Cl$_2$ solution was layered over 5 ml CCl$_4$ to yield violet crystals of 2 over a period of 2 weeks (yield 78%). *Anal.* Found: C, 42.2; H, 3.7; N, 9.9. Calc. for $C_{36}H_{28}N_8S_4Mo_2 \cdot CCl_4$ ($M = 1046.6$): C, 42.4; H, 2.7; N, 10.7%. FAB-MS: m/z (%) 894 (100) $[M^+ + H]$. IR: 1591s, 1497s, 1229w, 1137m, 1121m, 843w, 793m cm^{-1}. UV–Vis (CHCl$_3$): λ_{max} (ϵ(1 mol^{-1} cm^{-1})), 527 (424), 342 (1605), 327 (1641) nm.

$[Ru_2(monp)_4]$ (3)

0.354 g (0.75 mmol) Ru$_2$(OAc)$_4$Cl and 0.802 g (5 mmol) Hmonp were heated for 84 h in an argon atmosphere at 190 °C. Excess ligand was subsequently removed by sublimation and 25 ml CHCl$_3$ were added to the resulting solid. After filtration the solvent was removed and the product (3, yield 22%) dried in vacuum. Crystals of 3 suitable for an X-ray structural analysis were grown by gas diffusion of diethyl ether into a benzene solution of the product. *Anal.* Found: C, 51.6; H, 3.6; N, 12.8. Calc. for $C_{36}H_{28}N_8O_4Ru_2$ ($M = 838.8$): C, 51.6; H, 3.4; N, 13.4%. FAB-MS: m/z (%) 840.1 (100) $[M^+ + H]$. IR: 1630s, 1570s, 1438w, 1297w, 1262m, 1209w, 1144w, 1095m, 1022m, 842w, 803m, 782w cm^{-1}. UV–Vis (CHCl$_3$): λ_{max} (ϵ (1 mol^{-1} cm^{-1})), 800 (24), 451 (522), 338 (1739), 281 (2040), 313 (1675) nm.

Hmonp

Hmsnp

X-ray structural analyses of 1–3

Crystal and refinement data for **1–3** are summarised in Table 1. Unit cell constants were obtained from a least-squares fit to the settings of 25 reflections centred on a Siemens P4 diffractometer. Intensities were collected on the diffractometer at varied scan rates using Mo Kα radiation. Three selected reflections were monitored for each of the compounds during data collection; no significant alterations in intensity were observed. Semi-empirical absorption corrections were performed for each of the data sets on the basis of Ψ-scans. The structures were solved by Patterson and difference syntheses and refined by full-matrix least-squares. The asymmetric unit of **1** contains two disordered diethyl ether molecules (site occupation factors of 0.25 for O(11) and O(12), 0.5 for C(11)–C(14)), that of **2** two disordered CCl_4 molecules (site occupation factors of 0.5 for Cl(1)–Cl(4), 0.3 for Cl(1′)–Cl(4′) and 0.2 for Cl(5′)–Cl(8′)). Two benzene solvent molecules, the ring systems of which were refined as regular hexagons, are present in the asymmetric unit of complex **3**. Hydrogen atoms for the naphthyridine ring systems in **1–3** were included at geometrically calculated positions together with group isotropic temperature factors in the final refinement cycles. Anisotropic temperature factors were introduced for all non-hydrogen atoms in **1–3** with the exception of the disordered diethyl ether molecules in **1** and the second chloroform molecule (Cl(5′)–Cl(8′)) in **2**. Calculations were performed with the SHELXTL set of programmes (Siemens). Atom positional parameters with equivalent isotropic temperature factors for **1–3** are listed in Table 2.

Results and discussion

Reaction of $Mo(CO)_6$ with Hmonp in diglyme at 190 °C leads to the formation of the dimolybdenum(II) complex [$Mo_2(monp)_4$] (**1**) in 81% yield. As may be seen from Fig. 1 the four monoanionic ligands monp$^-$ in **1** bridge a quadrupole Mo–Mo bond and display the $1\kappa^1N{:}2\kappa^1O$ coordination mode. The complex exhibits crystallographic S_4 symmetry, which requires a *trans* arrangement of the Mo–N(1) and Mo–O(21) bonds. This *trans*-MoX$_2$Y$_2$ geometry about the individual molybdenum atoms is typical for dimolybdenum(II) complexes containing monoanionic bridging ligands with N,N, N,O, N,P and N,S donor sets [1]. Exceptions are provided by [$Mo_2(PhNpy)_4$] (PhNHpy = 2-anilinopyridine), in which *cis*-MoX$_2$Y$_2$ units are observed [11], and [$Mo_2(fhp)_4$]·thf (Hfhp = 2-hydroxy-6-fluoropyridine), which contains a polar quadrupole bond based on an O_4Mo–MoN$_4$ unit [12]. [$Mo_2(fhp)_4$]·thf also provides the only example of an axially coordinated solvent molecule for a dimolybdenum(II) complex Mo_2L_4 of a 2,6-disubstituted pyridine L. For both the *trans*- and *cis*-MoX$_2$Y$_2$ geometries, the non-coordinating groups or atoms in the 6-position (e.g. CH_3, PhNH, F, Cl) provide an effective steric shield for the potential axial binding sites of the Mo_2^{4+} units. An analogous role is adopted by the *trans*-sited naphthyridine nitrogens N8 and methyl groups in complex **1**. It is instructive to compare the molecular dimensions of **1** with those of [$Mo_2(mhp)_4$] (Hmhp = 2-hydroxy-6-methylpyridine) [13a], the X-ray structure of which has also been determined for its CH_3OH [13a] and CH_2Cl_2 solvates

TABLE 1. Crystal and refinement data

Compound	$1 \cdot 2(C_2H_5)_2O$	$2 \cdot 2CCl_4$	$3 \cdot 2C_6H_6$
Space group	$I4_1/a$	$C2/c$	$P2_1/n$
a (Å)	18.254(2)	22.988(5)	11.696(2)
b (Å)	18.254(2)	18.637(4)	19.530(4)
c (Å)	13.950(1)	17.110(3)	19.500(4)
β (°)	90	128.09(3)	104.11(3)
V (Å^3)	4648.3(6)	5769(2)	4320(1)
Z	4	4	4
M (g cm^{-1})	976.8	1200.4	995.0
D_c (g cm^{-3})	1.40	1.38	1.53
Crystal size (mm)	$0.58 \times 0.32 \times 0.20$	$0.50 \times 0.50 \times 0.38$	$0.32 \times 0.21 \times 0.20$
Radiation	Mo Kα	Mo Kα	Mo Kα
μ (cm^{-1})	5.8	9.7	7.4
Scan type	ω	ω	ω
$2\theta_{max}$ (°)	45	50	45
Reflections measured	1514	4853	5644
Reflections observed	802	2836	2957
Rejection criterion	$F_o^2 \leqslant 2\sigma(F_o^2)$	$F_o^2 \leqslant 2\sigma(F_o^2)$	$F_o^2 \leqslant 2\sigma(F_o^2)$
R	0.067	0.087	0.060
R_w	0.067	0.088	0.060
p	0.0003	0.00002	0.0008
Residual peaks (max./min.) (e Å^{-3})	0.49/$-$0.59	1.16/$-$0.98	0.68/$-$0.75

TABLE 2. Atom positional parameters ($\times 10^4$) with equivalent isotropic temperature factors ($\text{Å}^2 \times 10^3$)

Atom	x	y	z	U_{eq}[a]
1·2(C₂H₅)₂O				
Mo(1)	10000	2500	1999(1)	66(1)
N(1)	11123(8)	2945(7)	1958(16)	86(7)
C(2)	11412(10)	3041(9)	1069(19)	82(9)
O(21)	11070(7)	2893(6)	348(7)	66(5)
C(3)	12140(11)	3331(10)	1049(16)	96(9)
C(4)	12498(9)	3503(9)	1865(19)	93(9)
C(5)	12489(9)	3476(8)	3744(20)	103(9)
C(6)	12108(16)	3228(13)	4497(17)	118(12)
C(7)	11427(11)	2908(12)	4458(16)	111(12)
C(71)	11033(11)	2689(12)	5384(14)	122(10)
N(8)	11117(7)	2842(7)	3621(12)	73(6)
C(9)	11487(10)	3067(9)	2849(12)	60(7)
C(10)	12194(9)	3392(10)	2802(14)	63(7)
O(11)	9704(29)	−606(24)	−4324(32)	85(13)
O(12)	9829(22)	481(16)	−5596(23)	44(8)
C(11)	9521(25)	−170(26)	−4800(34)	146(16)
C(12)	8642(24)	−258(24)	−4764(31)	73(16)
C(13)	10621(20)	−373(19)	−4539(25)	96(11)
C(14)	11015(25)	241(22)	−5124(30)	154(15)
2·2CCl₄				
Mo(1)	5000	2959(1)	2500	50(1)
Mo(2)	5000	4102(1)	2500	49(1)
N(11)	5410(5)	4227(5)	4039(7)	53(6)
C(12)	5460(6)	3672(6)	4594(8)	54(7)
S(12)	5256(2)	2821(2)	4121(2)	62(2)
C(13)	5712(7)	3800(8)	5578(8)	60(8)
C(14)	5918(8)	4451(8)	5974(10)	75(10)
C(15)	6175(9)	5759(8)	5770(11)	91(11)
C(16)	6181(11)	6243(9)	5180(13)	97(14)
C(17)	5919(9)	6033(8)	4230(11)	86(12)
C(171)	5964(13)	6567(9)	3572(14)	123(18)
N(18)	5639(6)	5362(6)	3848(8)	73(8)
C(19)	5655(6)	4879(6)	4452(8)	49(7)
C(110)	5915(7)	5027(8)	5428(9)	65(8)
N(21)	6179(5)	2838(6)	3194(6)	50(6)
C(22)	6614(6)	3402(6)	3318(8)	53(7)
S(22)	6280(2)	4251(2)	3074(2)	59(2)
C(23)	7351(7)	3265(8)	3679(9)	61(9)
C(24)	7633(7)	2606(8)	3956(10)	71(10)
C(25)	7432(9)	1292(8)	4170(10)	79(10)
C(26)	6980(9)	811(9)	4143(10)	81(11)
C(27)	6276(8)	1019(7)	3782(9)	70(9)
C(271)	5746(10)	514(8)	3801(12)	106(13)
N(28)	6012(6)	1694(5)	3430(7)	60(7)
C(29)	6468(6)	2179(6)	3501(8)	47(7)
C(210)	7196(7)	2031(7)	3861(9)	63(8)
C(1)	1029(6)	3895(6)	1911(8)	85(19)
Cl(1)	839(4)	3339(4)	955(5)	85(5)
Cl(2)	1980(4)	3996(5)	2810(7)	124(6)
Cl(3)	594(8)	3584(8)	2398(9)	188(13)
Cl(4)	660(7)	4741(5)	1388(9)	182(12)
C(1′)	1891(5)	6435(5)	1099(7)	97(21)
Cl(1′)	1686(11)	6584(14)	−61(7)	198(19)
Cl(2′)	2608(8)	7012(7)	1973(8)	88(9)
Cl(3′)	2160(10)	5569(6)	1586(12)	191(15)
Cl(4′)	1151(6)	6775(8)	1052(11)	109(11)
Cl(5′)	2550(13)	7146(12)	1697(19)	101(5)
Cl(6′)	1424(14)	6512(21)	−187(9)	101(5)
Cl(7′)	1231(11)	6233(12)	1281(16)	101(5)
Cl(8′)	2423(13)	5647(9)	1315(19)	101(5)

(*continued*)

TABLE 2. (*continued*)

Atom	x	y	z	U_{eq}[a]
3·2C₆H₆				
Ru(1)	590(1)	682(1)	2372(1)	35(1)
Ru(2)	−655(1)	−192(1)	2414(1)	36(1)
N(11)	57(10)	644(5)	1256(5)	39(5)
C(12)	777(12)	966(7)	888(7)	47(7)
O(12)	1739(10)	1210(5)	1219(5)	68(5)
C(13)	325(15)	1034(8)	128(7)	63(8)
C(14)	−737(15)	790(7)	−185(7)	59(8)
C(15)	−2563(13)	158(8)	−93(7)	65(7)
C(16)	−3165(13)	−191(8)	333(7)	59(7)
C(17)	−2659(10)	−272(7)	1055(6)	44(6)
C(171)	−3319(14)	−663(8)	1497(7)	68(7)
N(18)	−1578(9)	3(5)	1353(5)	36(5)
C(19)	−1003(11)	370(6)	931(6)	43(6)
C(110)	−1453(12)	445(7)	197(6)	50(7)
N(21)	1054(10)	686(6)	3476(5)	45(5)
C(22)	1621(12)	1255(7)	3813(7)	58(7)
O(22)	1752(10)	1753(5)	3438(5)	69(5)
C(23)	2080(15)	1207(8)	4577(7)	66(8)
C(24)	1972(14)	648(8)	4941(8)	66(7)
C(25)	1162(15)	−530(8)	4927(7)	72(8)
C(26)	513(14)	−1061(8)	4542(7)	68(8)
C(27)	42(13)	−988(6)	3816(7)	54(7)
C(271)	−656(15)	−1560(7)	3405(8)	70(8)
N(28)	240(9)	−400(5)	3483(5)	37(4)
C(29)	898(11)	127(6)	3858(6)	44(6)
C(210)	1352(14)	77(7)	4593(6)	59(7)
N(31)	499(10)	−849(5)	2058(5)	39(5)
C(32)	85(13)	−1482(6)	1804(7)	47(7)
O(32)	−999(10)	−1592(5)	1697(5)	66(5)
C(33)	939(16)	−1974(8)	1674(8)	68(9)
C(34)	2068(16)	−1811(7)	1758(7)	67(9)
C(35)	3632(14)	−921(8)	2077(8)	61(8)
C(36)	3932(13)	−249(9)	2295(8)	70(8)
C(37)	3091(12)	207(8)	2422(7)	59(7)
C(371)	3419(13)	922(7)	2665(9)	66(7)
N(38)	1954(11)	−11(5)	2334(5)	38(5)
C(39)	1646(12)	−679(6)	2129(6)	43(6)
C(310)	2473(14)	−1149(7)	1993(7)	52(7)
N(41)	−1725(10)	492(6)	2793(5)	44(5)
C(42)	−2530(13)	220(8)	3123(7)	62(8)
O(42)	−2606(11)	−410(6)	3184(6)	73(5)
C(43)	−3287(13)	690(10)	3386(8)	76(8)
C(44)	−3201(16)	1363(10)	3297(9)	82(9)
C(45)	−2225(15)	2343(8)	2821(8)	76(9)
C(46)	−1375(15)	2548(8)	2471(9)	78(9)
C(47)	−624(13)	2074(7)	2263(7)	62(7)
C(471)	314(15)	2307(8)	1911(8)	69(8)
N(48)	−735(11)	1397(5)	2422(6)	46(5)
C(49)	−1634(13)	1182(7)	2722(7)	50(7)
C(410)	−2364(14)	1651(8)	2960(8)	61(8)
C(51)	6907(15)	1357(17)	6102(7)	152(19)
C(52)	6869	1982	5750	147(17)
C(53)	6027	2091	5117	134(16)
C(54)	5222	1576	4837	115(13)
C(55)	5261	951	5188	135(16)
C(56)	6103	842	5821	160(20)
C(61)	5196(36)	2125(7)	−308(7)	125(14)
C(62)	6318	1955	94	131(17)
C(63)	6451	1650	756	110(14)
C(64)	5463	1516	1016	135(16)
C(65)	4341	1687	613	137(17)
C(66)	4208	1991	−49	133(16)

[a]Equivalent isotropic temperature factors U_{eq} are defined as one third of the trace of the orthogonalised U_{ij} tensor.
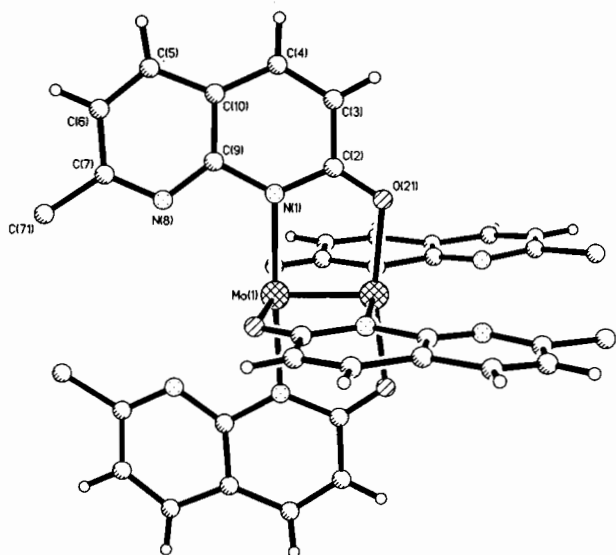
Fig. 1. Molecular structure of [Mo$_2$(monp)$_4$] (1). Selected bond distances (Å) and angles (°): Mo(1)–Mo(1a) 2.090(4), Mo(1)–N(1) 2.20(1), Mo(1)–O(21a) 2.09(1), C(2)–O(21) 1.21(3); N(1)–Mo(1)–Mo(1a) 88.5(6), O(21a)–Mo(1)–Mo(1a) 95.9(3), N(1)–Mo(1)–N(1a) 177(1), N(1)–Mo(1)–O(21a) 91.6(5), N(1)–Mo(1)–O(21b) 88.7(5), O(21a)–Mo(1)–O(21b) 168.3(6).

Fig. 2. Molecular structure of [Mo$_2$(msnp)$_4$] (2). Selected bond distances (Å) and angles (°): Mo(1)–Mo(2) 2.131(2), Mo(1)–S(12) 2.468(4), Mo(1)–N(21) 2.200(11), Mo(2)–S(22) 2.477(4), Mo(2)–N(11) 2.195(12), C(12)–S(12) 1.709(12), C(22)–S(22) 1.694(12); Mo(2)–Mo(1)–S(12) 96.0(1), Mo(2)–Mo(1)–N(21) 95.9(3), S(12)–Mo(1)–N(21) 91.3(3), S(12)–Mo(1)–N(21a) 87.5(3), S(12)–Mo(1)–S(12a) 168.1(2), N(21)–Mo(1)–N(21a) 168.2(5), Mo(1)–Mo(2)–N(11) 96.1(3), Mo(1)–Mo(2)–S(22) 96.4(1), N(11)–Mo(2)–S(22) 89.2(3), N(11)–Mo(2)–N(11a) 167.9(5), S(22)–Mo(2)–S(22a) 167.2(2), S(22)–Mo(2)–N(11) 89.2(3), S(22)–Mo(2)–N(11a) 89.4(3).

[13b]. The Mo–Mo distances of 2.067(1), 2.068(1) and 2.065(1) Å in [Mo$_2$(mhp)$_4$] and its respective solvates are among the shortest known [1]. A significantly longer Mo–Mo bond length of 2.090(4) Å is observed for complex 1, which is in accordance with a reduction in the basicity of the ring nitrogen N1 in monp$^-$ in comparison to mhp$^-$. For instance a similar Mo–Mo distance of 2.085(1) Å is exhibited by [Mo$_2$(chp)$_4$] (Hchp = 2-hydroxy-6-chloropyridine) [14], for which the inductive effect of the substituent Cl (versus CH$_3$) will influence the basicity of the pyridine nitrogen. The Mo(1)–N(1) distance of 2.20(1) Å is longer than the average value of 2.17(1) observed for [Mo$_2$(mhp)$_4$] and its CH$_3$OH and CH$_2$Cl$_2$ solvates. A recent X-ray structural study of 5,7-dimethyl-1,8-naphthyridin-2-one [15] has provided an exocyclic C–O distance of 1.245(2) Å indicating that the pyridone tautomer is predominant. This is also the case in the dimolybdenum(II) complex 1, which exhibits an effectively ketonic C(2)–O(21) bond length of 1.21(3) Å. The trans-sited naphthyridine ring systems in 1 display only a small deviation from coplanarity as evidenced by their interplanar dihedral angle of −4.8° and the torsion angle N(1)–Mo(1)–Mo(1a)–O(21) of −1.4°.

The 1$\kappa^1 N$:2$\kappa^1 S$ coordinated dimolybdenum(II) complex [Mo$_2$(msnp)$_4$] (2) may be prepared in 78% yield in an analogous manner to 1 by reaction of Mo(CO)$_6$ with Hmsnp in diglyme at 190 °C. 2 exhibits crystallographic C$_2$ symmetry with the monoanionic ligands msnp sited trans to one another (Fig. 2). As a result

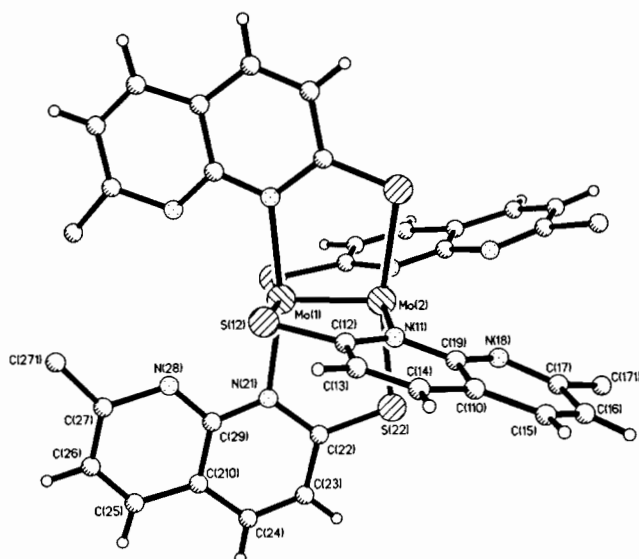of the fact that the Mo–S distances of 2.468(4) and 2.477(4) Å are on average 0.275 Å longer than the Mo–N distances of 2.195(12) and 2.200(11) Å, the naphthyridine rings are tilted towards the C$_2$ axis of the complex, which contains the Mo(1)–Mo(2) bond. In order to prevent extremely short non-bonded C…C contacts between the methyl carbon atoms of trans-sited monoanionic ligands, the naphthyridine rings are forced to twist away from a common plane, which would contain the Mo–Mo quadrupole bond. The degree of twisting may be gauged from the interplanar dihedral angles of 29.8 and 25.0° for ligands symmetry related by the C$_2$ axis and by the S(12)–Mo(1)–Mo(2)–N(11) and S(22)–Mo(2)–Mo(1)–N(21) torsion angles of 8.9 and 7.0°. S(12) and S(22) are displaced 0.27 and 0.26 Å from the best least-squares planes of their respective naphthyridine ring systems. Despite the relatively large degree of twist displayed by the ligands in 2, the C(171)…C(171a) and C(271)…C(271a) distances of 3.62 and 3.57 Å between methyl carbon atoms in trans-positioned ligands are still markedly shorter than the analogous C(71)…C(71a) distance of 3.83 Å in 1.

The molecular dimensions of [Mo$_2$(msnp)$_4$] (2) may be compared with those of [Mo$_2$(dmmp)$_4$] (Hdmmp = 4,6-dimethyl-2-mercapto-pyrimidine) [16]

and [Mo$_2$(2-mq)$_4$] (2-mqH = 2-mercaptoquinoline) [17] which also display $1\kappa^1N{:}2\kappa^1S$ coordination. It is interesting to note that the Mo–Mo quadrupole bond length of 2.131(2) Å in **2** is significantly longer than those of 2.083(2) and 2.089(1) Å in [Mo$_2$(dmmp)$_4$] and [Mo$_2$(2-mq)$_4$]. In contrast the Mo–N and Mo–S distances (av. values 2.20(1) and 2.472(5) Å) are more similar to those in the above dimolybdenum(II) complexes. These display average Mo–N bond lengths of 2.20(1) and average Mo–S bond lengths of 2.455(5) and 2.449(5) Å, respectively. Cotton has suggested that it is possible that the slightly longer Mo–Mo distances in N,S coordinated complexes [Mo$_2$L$_4$] in comparison to the analogous N,O coordinated complexes may be attributed to the longer N...X separation (X = S,O) in the former [16].

[Ru$_2$(monp)$_4$] (**3**) was isolated in relatively low yield (22%) from the solid state reaction of Ru$_2$(OAc)$_4$Cl and Hmonp at 190 °C. In contrast to complex **1** the four bridging monoanionic ligands monp$^-$ in **3** display a $1\kappa^1N{:}2\kappa^1N'$ coordination mode (Fig. 3). This is the
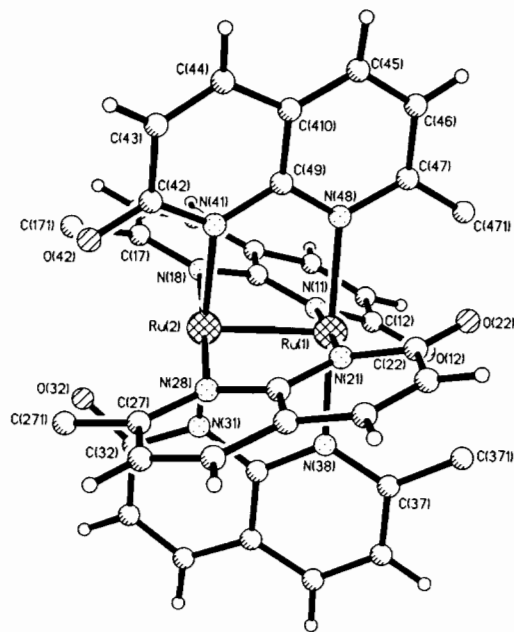

Fig. 3. Molecular structure of [Ru$_2$(monp)$_4$] (**3**). Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.258(2), Ru(1)–N(11) 2.112(9), Ru(1)–N(21) 2.088(9), Ru(1)–N(38) 2.106(12), Ru(1)–N(48) 2.107(12), Ru(2)–N(18) 2.121(9), Ru(2)–N(28) 2.132(10), Ru(2)–N(31) 2.099(12), Ru(2)–N(41) 2.087(12); Ru(2)–Ru(1)–N(11) 88.8(3), Ru(2)–Ru(1)–N(21) 88.5(3), Ru(2)–Ru(1)–N(38) 90.9(3), Ru(2)–Ru(1)–N(48) 90.6(3), N(11)–Ru(1)–N(21) 177.3(5), N(11)–Ru(1)–N(38) 88.7(4), N(11)–Ru(1)–N(48) 92.0(4), N(21)–Ru(1)–N(38) 91.7(4), N(21)–Ru(1)–N(48) 87.6(4), N(38)–Ru(1)–N(48) 178.3(4), Ru(1)–Ru(2)–N(18) 90.5(3), Ru(1)–Ru(2)–N(28) 90.7(3), Ru(1)–Ru(2)–N(31) 88.7(3), Ru(1)–Ru(2)–N(41) 88.7(3), N(18)–Ru(2)–N(28) 178.7(4), N(18)–Ru(2)–N(31) 90.2(4), N(18)–Ru(2)–N(41) 91.4(4), N(28)–Ru(2)–N(31) 90.3(4), N(28)–Ru(2)–N(41) 88.2(4), N(31)–Ru(2)–N(41) 177.0(4).

first example of a diruthenium(II) complex of the type [Ru$_2$L$_4$] in which N,N' coordinated naphthyridine ring systems bridge an Ru–Ru double bond. As for complexes **1** and **2** a *trans*-MX$_2$Y$_2$ geometry is observed for the individual metal atoms (M = Ru) in **3**. The *trans*-sited ligands in this complex twist away from a common plane, which would contain the Ru–Ru double bond, in order to lengthen the non-bonded O...C contacts between the ketonic oxygen and methyl carbon atoms of neighbouring *cis*-sited ligands. Apposite distances, which underline the shortness of these interactions, are: O(12)...C(371) 3.07, O(12)...C(471) 3.20, O(22)...C(371) 3.19, O(22)...C(471) 3.23, O(32)... C(171) 3.20, O(32)...C(271) 3.26, O(42)...C(171) 3.23, O(42)...C(271) 3.16 Å. Interplanar dihedral angles of 36.5 and 36.3° are observed for those monoanionic ligands in *trans* position to one another. The extreme degree of twist from the eclipsed conformation in complex **3** may also be gauged from the following torsion angles (χ): N(11)–Ru(1)–Ru(2)–N(18) − 18.1, N(21)–Ru(1)–Ru(2)–N(28) − 18.2, N(31)–Ru(2)–Ru(1)–N(38) − 16.7, N(41)–Ru(2)–Ru(1)–N(48) − 17.7°.

The Ru–Ru distance of 2.258(2) Å in **3** falls within the range (2.235(1)–2.28(2) Å) [1] observed for Ru$_2$$^{4+}$ complexes with carboxylate or 2,6-pyridinate bridges. For instance the metal–metal bond length is 2.35(1) in the orthorhombic modification of Ru$_2$(mhp)$_4$ and 2.259(1) Å in Ru$_2$(bhp)$_4$ [18] (Hbhp = 2-hydroxy-6-bromopyridine), both of which display an approximately D_{2d} symmetry, as is the case for **3**. The average twist angles χ for these complexes are 6.2 and 1.2°, respectively. In contrast much larger twist angles similar to those in **3** are observed in the two polar Ru$_2$$^{4+}$ units of [Ru$_2$(chp)$_4$]$_2$ [18]. In this complex two Ru$_2$(chp)$_4$ moieties, in each of which there are three pyridine ligands pointing in the same direction, are linked through bridging oxygen atoms, which each occupy an axial coordination site of the other Ru$_2$$^{4+}$ unit. This arrangement leads to steric crowding of three chlorine atoms at the ends of the molecule with the result that χ values in the range 15.4–22.7° are observed. The Ru–Ru distance of 2.28(1) Å in the naphthyridine bridged complex [Ru$_2$(OAc)$_3$(μ-dpnp)]PF$_6$ [5a] is slightly longer than that in **3**.

There has been considerable discussion concerning the ground state in diruthenium(II) complexes Ru$_2$L$_4$ [1, 18, 19] for which both the $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ and $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*2}$ electronic configurations may be formulated. However the fact that the Ru–Ru bond lengths in Ru$_2$L$_4$ complexes are essentially the same as those in cations of the type [Ru$_2$(O$_2$CR)$_4$]$^+$, for which $\sigma^2\pi^4\delta^2\pi^{*2}\delta^*$ configuration is certain, provides clear structural evidence for the $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*2}$ configuration, which may also be assumed for **3**. The temperature

dependence of the magnetic susceptibilities of the complexes [Ru$_2$(mhp)$_4$], [Ru$_2$(chp)$_4$] and [Ru$_2$(bhp)$_4$] is also in accordance with the latter configuration [18], which gives rise to a ^{3}A$_{2g}$ state. Zero-field splitting of this state yields a singlet ($M_s = 0$) state lying several hundred wave numbers below an $M_s = \pm 1$ state. As a result the observed magnetic moment tends towards zero as the temperature approaches 0 K. The magnetic moments μ_{eff} of these complexes lie in the range 2.2–2.8 BM at 293 K. [Ru$_2$(monp)$_4$] **3** displays a similar magnetic behaviour with a μ_{eff} value of 2.51 BM at room temperature.

It is not immediately apparent why **3** exhibits the $1\kappa^1N{:}2\kappa^1N'$ coordination mode in contrast to the $1\kappa^1N{:}2\kappa^1O$ mode of the dimolybdenum(II) complex **1**, in particular as the former mode leads to extreme steric crowding of the 2- and 7-substituents of the monoanionic ligands. The solid state reaction of Ru$_2$(OAc)$_4$Cl with Hmonp allows the isolation of **3** in only 22% yield. As has been demonstrated for 2,6-substituted pyridines [18] it seems likely that the use of Ru$_2$(OAc)$_4$ should lead to a marked improvement in this yield and work is in progress in this respect.

Acknowledgements

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