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Diruthenium complexes with 5-methyl-7-phenyl-1,8-naphthyridin-2-one as an ambidentate bridging ligand

Markus Mintert, William S. Sheldrick

Lehrstuhl für Analytische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

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Abstract

Reaction of $[Ru_2Cl(OAc)_4]$ with mphonp$^-$ (Hmphonp = 5-methyl-7-phenyl-1,8-naphthyridin-2-one) in methanol at reflux leads to precipitation of the diruthenium(II,III) complex $[Ru_2Cl(mphonp)_2(OAc)_2]$ (**1**) within 0.5 h. The compound exhibits a polar arrangement of ligands with Ru(1) coordinated by two *trans*-sited mphonp N1 atoms, Ru(2) by two *trans*-sited mphonp O2 atoms and the axial chloride ligand. **1** is reduced to the diruthenium(II,II) complex $[Ru_2(mphonp)_2(OAc)_2]$ (**2**) on further refluxing (6 h). In contrast to **1**, the *trans*-sited mphonp$^-$ ligands now display the N,N′ coordination mode and point in opposite directions. The further reaction of **2** with mphonp$^-$ in refluxing methanol (36 h) then leads to substitution of all four acetate ligands and the formation of $[Ru_2(mphonp)_4]$ (**3a**). Steric interactions between adjacent phenyl substituents appear to be responsible for the adoption of the electronically less preferred N,O coordination mode by three of the bridging ligands in the polar water adduct $[Ru_2(mphonp)_4(H_2O)]$ (**3b**). Hmphonp, **1**, **2** and **3b** were characterised by X-ray structural analysis.

Keywords: Ruthenium complexes; Substituted naphthyridine complexes; Crystal structures; Dinuclear complexes

1. Introduction

Although 1,8-naphthyridine (np) has beeen demonstrated to act as a dinucleating ligand capable of bridging metal–metal bonds in the complexes $[Ni_2Br_2(np)_4]BPh_4$ [1a] and $[Rh_2(np)_4]Cl_4$ [1b], it has more generally been observed to function as a mono- or bidentate ligand in mononuclear complexes such as $[CuCl_2(np)_2]$ [2a], $[PtCl(np)(PEt_3)_2]BF_4$ [2b], $[Cd(np)_4](ClO_4)_2$ [2c] or $[Fe(np)_4](ClO_4)_2$ [2d]. However, in the past decade a range of dinuclear compounds containing bridging 2,7-substituted 1,8-naphthyridines has been reported. These include dirhodium(II) complexes of the type $[Rh_2(OAc)_3L]PF_6$, which exhibit crescent-shaped ligands L such as dpnp (2,7-bis(2-pyridyl)-1,8-naphthyridine) [1b,3a–c]. The ligand dpnp was also recently employed in the preparation of $[Ru_2Cl_2(bpy)_2(\mu\text{-dpnp})](PF_6)_2$ and $[Ru_2(OAc)_3(\mu\text{-dpnp})]PF_6$, both of which contain an Ru_2^{4+} core and axially coordinating dpnp pyridine rings [4a]. Both the latter complex and the structurally analogous Ru_2^{5+} species $[Ru_2(OAc)_3(\mu\text{-dcnp})]$ (dcnp = 1,8-naphthyridine-2,7-dicarboxylate) [4] were characterised by X-ray structural analysis. A tetranuclear complex $[\{Mo_2(O_2C\text{-t-Bu})_3\}_2(\mu\text{-donp})]\cdot 2thf$ (H_2donp = 1,8-naphthyridin-2,7-dione), containing two discrete Mo–Mo quadruple bonds of length 2.10 Å in close proximity at a central Mo–Mo distance of 3.17 Å, has been studied by Chisholm and co-workers as a molecular model for building blocks of stiff-chain polymers [5a,b].

We have recently described the dimolybdenum(II) complexes $[Mo_2(monp)_4]$ and $[Mo_2(msnp)_4]$ (Hmonp = 7-methyl-1,8-naphthyridin-2-one, Hmsnp = 7-methyl-1,8-naphthyridin-2-thione), which were synthesised by the reaction of $Mo(CO)_6$ with the appropriate naphthyridine derivative in diglyme at 190 °C [6]. Four monoanionic ligands bridge the quadruple Mo–Mo bonds in these N,O dinuclear complexes and display respectively analogous N,S coordination modes. *Trans*-MoN_2X_2 geometries (X = O, S) are observed for the individual Mo atoms leading to steric crowding of mutually *trans*-sited 7-methyl substituents in $[Mo_2(msnp)_4]$, which is alleviated by a twisting distortion of the $[msnp]^-$ ligands with an average torsion angle of 8.0°. In contrast, the solid-state reaction of $[Ru_2Cl(OAc)_4]$ with Hmonp at 190 °C leads to the formation of $[Ru_2(monp)_4]$ in which N,N′ coordinated naphthyridine ring systems bridge an Ru–Ru double bond. Once again, a *trans*-MN_2X_2 geometry (X = N′) is displayed by the individual metal atoms (M = Ru). In this case, however, a much greater average twist of 17.7° from the eclipsed conformation is observed for the naphthyridine ring systems, this being necessary in order to reduce steric repulsions between the ketonic oxygen and

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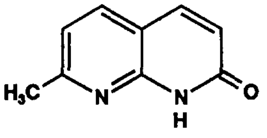
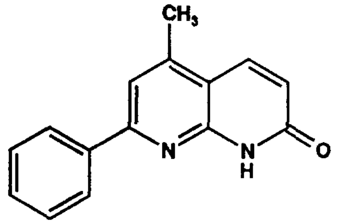
methyl carbon atoms of neighbouring *cis*-sited [monp]$^-$ ligands. The values of the twist angle in Mo_2L_4 and Ru_2L_4 complexes will, of course, to some extent be dependent on the order of the metal–metal bond.



Hmonp



Hmphonp

The above findings prompted us to investigate the structures of dinuclear [mphonp]$^-$ complexes (Hmphonp = 5-methyl-7-phenyl-1,8-naphthyridin-2-one) with the goal of understanding the role of electronic and steric factors in the adoption of a particular coordination mode by such potentially ambidentate bridging ligands. Molecular modelling indicates that the introduction of a 7-phenyl-substituent should lead to a further increase in steric crowding of *cis*-sited 2- and 7-substituents for [mphonp]$^-$ in comparison to [monp]$^-$, which would be expected to prevent the formation of a uniquely N,N′ coordinated dinuclear complex $[Ru_2(mphonp)_4]$. In contrast, twisting of the naphthyridine planes should allow the formation of N,O coordinated species $[M_2(mphonp)_4]$ with either *cis*- or *trans*-MN_2O_2 geometries at the individual metal atoms M. We have now studied the reaction of $[Ru_2(OAc)_4Cl]$ with Hmphonp in methanol at reflux which leads to a rapid precipitation of $[Ru_2Cl(mphonp)_2(OAc)_2]$ (**1**) within 0.5 h. Both the reduction of the Ru_2^{5+} core to Ru_2^{4+} in $[Ru_2(mphonp)_2(OAc)_2]$ (**2**) and the subsequent substitution of the remaining bridging acetate ligands to yield $[Ru_2(mphonp)_4]$ (**3a**) take place by slow heterogeneous reaction. We now report the preparation and X-ray structural characterization of **1**–**3b**.

2. Experimental

All solvents were dried and distilled under argon before use. IR spectra were recorded as KBr discs on a Perkin-Elmer 1760 spectrometer and electronic spectra on a Perkin-Elmer Lambda 15. ^{1}H NMR spectra were registered on a Bruker AM 400 with values reported as ppm relative to the signal of the relevant deuterated solvent. FAB mass spectra were measured on a VG Autospec employing 3-nitrobenzyl alcohol as the matrix. Elemental analyses were performed on a Carlo Erba 1106.

2.1. Preparation of Hmphonp and its complexes 1–3

2.1.1. 5-Methyl-7-phenyl-1,8-naphthyridin-2-one (Hmphonp)

The synthesis of Hmphonp was performed by adaption of literature methods [7] for other naphthyridine derivatives. 11 g (101 mmol) 2,6-diaminopyridine and 15.9 g (98 mmol) 1-benzoyl acetone were heated at 90 °C with stirring for 3 h in 100 ml of 85% H_3PO_4. The solution was neutralised with aqueous NH_3 and the product, 2-amino-5-methyl-7-phenyl-1,8-naphthyridine, $H_2mphNnp$, extracted with $CHCl_3$. Removal of the solvent afforded 18.3 g of $H_2mphNnp$ (79% yield). 14.8 g (174 mmol) KNO_2 in 15 ml H_2O were then slowly added to 18 g (76 mmol) of $H_2mphNnp$ in 100 ml of 40% H_2SO_4 at − 10 °C. After stirring for 1 h at this temperature, the solution was allowed to reach room temperature and then heated for 20 min at 80 °C. Neutralisation with aqueous NH_3 followed at 0 °C and the product was subsequently extracted with $CHCl_3$. After removal of the solvent the solid was recrystallised from toluene to afford 15.1 g of Hmphonp (84% yield). Crystals of $[H_2mphonp]Cl$ were obtained by slow evaporation of a concentrated HCl solution of the ligand.

Anal. Found: C, 76.6; H, 5.4; N, 12.5. Calc. for $C_{15}H_{11}N_2O$ (M = 236.3): C, 76.3; H, 5.1; N, 11.9%. ^{1}H NMR (d_6-DMSO): 2.62 (s, 3H, CH_3), 6.55 (d, 1H, H3), 7.40–7.64 (m, 3H, C_6H_6), 7.70 (s, 1H, H6), 8.06 (d, 1H, H4), 8.05–8.30 (m, 2H, C_6H_5) ppm. IR: 3048m, 1662s, 1585s, 1534m, 1445w, 1146w, 865m, 831m, 774s, 701s cm^{-1}.

2.1.2. $[Ru_2Cl(mphonp)_2(OAc)_2]$ (1)

0.237 g (1 mmol) Hmphonp in 25 ml methanol was stirred with 1 ml 1 M NaOMe/HOMe under argon to yield a deep brown solution. Addition of 0.118 g (0.25 mmol) of $[Ru_2Cl(OAc)_4]$ followed by stirring at reflux led to precipitation of **1** within 0.5 h. The violet product was filtered off and washed with diethyl ether (yield 72%). Suitable crystals of **1** were grown by slow gas phase diffusion of pentane into a $CHCl_3$ solution of the product. *Anal.* Found: C, 50.1; H, 3.6; N, 6.2. Calc. for $C_{34}H_{28}N_4O_6ClRu_2$ (M = 826.2) C, 49.4; H, 3.4; N, 6.8%. FAB-MS: m/z (%) 791 (100) $[M-Cl]^+$. IR: 2921w, 2792w, 1577s, 1506m, 1431s, 1375m, 1143w, 1046m, 769w, 519w cm^{-1}. UV–Vis ($CHCl_3$): λ_{max} (ϵ (l mol cm^{-1}) 448 (9.44×10^3), 317 (27.79×10^3).

2.1.3. $[Ru_2(mphonp)_2(OAc)_2]$ (2)

The reaction between Hmphonp and $[Ru_2Cl(OAc)_4]$ was carried out under identical conditions to those used for the preparation of **1**. In this case refluxing was continued for a total of 6 h during which time the colour of the precipitate changed from violet to brown. After filtration the solid was washed with diethyl ether to afford a mixture of **2** and **3** (total yield 83%). Suitable crystals of **2** (yield 20%) were grown by fractional crystallisation employing slow vapour diffusion of pentane into a chloroform solution of the product. *Anal.* Found: C, 52.3; H, 3.1; N, 7.3. Calc. for $C_{34}H_{28}N_4O_6Ru_2$

(M=790.8): C, 51.6; H, 3.6; N, 7.1%. FAB-MS: m/z (%) 792 (100) $[M+H]^+$. IR: 3057w, 1578s, 1435s, 1366m, 1141m, 1014w, 768w cm^{-1}. UV–Vis ($CHCl_3$): λ_{max} (ϵ (1 mol cm^{-1}) 450 (7.23×10^3), 319 (21.80×10^3).

2.1.4. *[$Ru_2(mphonp)_4$] (3a)*

Employing identical initial conditions as for the preparation of **1** refluxing was continued in this case for a total of 36 h. After filtration the brown product was washed with diethyl ether to give **3** in 89% yield. *Anal.* Found: C, 62.0; H, 4.3; N, 9.2. Calc. for $C_{60}H_{44}N_8O_4Ru_2$ (M=1143.2): C, 63.0; H, 3.9; N, 9.8%. FAB-MS: m/z (%) 1144 (100) $[M+H]^+$. IR: 3057w, 1618s, 1577s, 1511s, 1496s, 1353m, 1141s, 769m, 697m, 623m cm^{-1}. UV–Vis ($CHCl_3$): λ_{max} (ϵ (1 mol cm^{-1}) 462 (4.83×10^3), 329 (19.45×10^3). Crystals of [$Ru_2(mphonp)_4(H_2O)$] (**3b**) were grown in very low yield (8 mg) by slow vapour diffusion of hexane into an *ortho*-dichlorobenzene solution of the product. The latter solution is assumed to have been slightly wet, thereby providing the axially coordinated water molecules in **3b**.

2.2. *X-ray structural analyses of [$H_2mphonp$]Cl and 1–3*

Crystal and refinement data 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 the course of data collection; no significant alterations in intensity were recorded. Semi-empirical absorption corrections were performed for each of the data sets on the basis of ψ scans. The structures were solved by Patterson syntheses or direct methods and refined by full-matrix least-squares for [$H_2mphonp$]Cl, **1** and **2** on F and for **3** on F^2 [8]. Hydrogen atoms in **1–3** were included at geometrically calculated positions together with group isotropic temperature factors in the final refinement cycles. Calculations were performed with the SHELXTL set of programs (Siemens) and for **3** with SHELXL-93 [8]. Atom positional parameters with equivalent isotropic temperature factors are listed in Table 2. See also Section 4.

3. Results and discussion

The structure of [$H_2mphonp$]Cl is depicted in Fig. 1. Reaction of Hmphonp with [$Ru_2Cl(OAc)_4$] in methanol at reflux leads to rapid precipitation of the discrete diruthenium(II,III) complex [$Ru_2Cl(mphonp)_2(OAc)_2$] (**1**) within 0.5 h. As may be seen from Fig. 2 the two *trans*-sited monoanionic ligands mphonp$^-$ exhibit the N,O coordination mode, in contrast to the 7-methyl substituted 1,8-naphthyridin-2-one ligands monp$^-$ in [$Ru_2(monp)_4$], for which the N,N′ coordination mode is observed [6]. An analogous structure to that of **1** has previously been established for the mixed ligand complex [$Ru_2Cl(mhp)_2(OAc)_2$] (Hmhp = 6-methylpyridin-2-one) characterised by Cotton and co-workers [9]. Both complexes exhibit a polar arrangement of the bridging ligands as has been observed in other

Table 1
Crystal and refinement data

Compound	[$H_2mphonp$]Cl	$1\cdot3CHCl_3$	$2\cdot2CHCl_3$	$3\cdot1.5C_6H_4Cl_2\cdot0.5CH_3OH$
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	9.108(2)	10.990(3)	12.029(3)	15.923(3)
b (Å)	7.508(2)	15.312(6)	10.886(3)	16.328(3)
c (Å)	19.365(4)	15.337(7)	15.827(4)	16.898(3)
α (°)	90	97.55(3)	90	106.31(3)
β (°)	102.77(3)	108.90(3)	105.20(2)	97.66(3)
γ (°)	90	104.98(3)	90	116.37(3)
V (Å^3)	1291.6(5)	2293(1)	1999.9(9)	3604(1)
Z	4	2	2	2
M	272.7	1184.3	514.7	1395.7
D_c (g cm^{-3})	1.40	1.72	1.71	1.29
Crystal size (mm)	0.32×0.34×0.74	0.14×0.40×0.50	0.10×0.30×0.70	0.10×0.14×0.43
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (cm^{-1})	2.9	12.9	12.0	5.8
Scan type	ω	ω	ω	ω
$2\theta_{max}$ (°)	45	55	45	45
Reflections measured	1678	7406	2579	9365
Reflections observed	1222	5459	1897	2601
Rejection criterion	$F_o^2\le2\sigma(F_o^2)$	$F_o^2\le2\sigma(F_o^2)$	$F_o^2\le2\sigma(F_o^2)$	$F_o^2\le2\sigma(F_o^2)$
R	0.050	0.043	0.066	0.083
R_w	0.050	0.044	0.074	0.209 [a]
p	0.0002	0.0001		
Residual peaks: max., min. (e Å^{-3})	0.34, −0.22	0.94, −0.84	2.21, −0.99	1.40, −0.55

[a] $wR2$ for refinement on F^2.

Table 2
Atom positional parameters (× 10^4) with equivalent isotropic temperature factors ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
[H_2mphonp]Cl				
Cl	8015(1)	2264(2)	1152(1)	55(1)
N(1)	691(3)	−1895(5)	2221(2)	43(1)
C(2)	−578(4)	−2168(7)	1686(2)	47(2)
O(2)	−1734(3)	−2718(5)	1832(2)	64(1)
C(3)	−389(5)	−1728(7)	984(2)	50(2)
C(4)	936(5)	−1205(7)	858(2)	46(2)
C(5)	3664(4)	−435(6)	1348(2)	39(2)
C(51)	3982(6)	10(9)	641(3)	60(2)
C(6)	4801(5)	−322(6)	1942(2)	41(2)
C(7)	4560(4)	−657(6)	2608(2)	36(2)
C(71)	5710(4)	−487(6)	3271(2)	37(2)
C(72)	7192(5)	−988(6)	3294(3)	46(2)
C(73)	8250(5)	−873(7)	3915(3)	56(2)
C(74)	7852(5)	−196(7)	4513(3)	56(2)
C(75)	6400(5)	314(6)	4495(2)	47(2)
C(76)	5326(5)	168(6)	3876(2)	41(2)
N(8)	3166(3)	−1153(5)	2664(2)	15(1)
C(9)	2051(4)	−1329(5)	2106(2)	36(2)
C(10)	2219(4)	−969(6)	1419(2)	38(2)
1·3$CHCl_3$				
Ru(1)	341(1)	3590(1)	2561(1)	30(1)
Ru(2)	2037(1)	4761(1)	2470(1)	33(1)
Cl	3872(2)	6045(1)	2416(1)	45(1)
O(1)	2139(4)	3861(3)	1415(3)	43(2)
O(2)	617(4)	2687(2)	1613(2)	38(2)
C(1)	1456(7)	3007(4)	1230(4)	42(3)
C(2)	1634(8)	2345(4)	497(5)	69(4)
O(3)	1847(4)	5631(2)	3496(2)	40(2)
O(4)	79(4)	4507(2)	3501(2)	35(2)
C(3)	866(7)	5347(4)	3768(3)	37(3)
C(4)	627(7)	6050(4)	4417(4)	56(3)
N(11)	−1001(5)	3909(3)	1455(3)	31(2)
C(12)	−578(6)	4676(4)	1156(3)	33(3)
O(12)	695(4)	5163(3)	1512(2)	39(2)
C(13)	−1490(6)	4955(4)	445(3)	38(3)
C(14)	−2807(7)	4431(4)	51(4)	42(3)
C(15)	−4618(6)	2966(4)	−75(4)	41(3)
C(151)	−5745(7)	13180(5)	−816(4)	66(4)
C(16)	−4881(6)	2160(4)	230(4)	44(3)
C(17)	−3876(6)	1961(4)	933(4)	36(3)
C(171)	−4166(7)	1065(4)	1220(4)	42(3)
C(172)	−3139(7)	737(4)	1656(4)	58(3)
C(173)	−3410(8)	−99(5)	1922(5)	71(4)
C(174)	−4701(9)	−607(5)	1755(5)	71(4)
C(175)	−5735(9)	−296(5)	1338(6)	86(5)
C(176)	−5483(8)	542(5)	1063(5)	68(4)
N(18)	−2606(5)	2551(3)	1339(3)	34(2)
C(19)	−2337(6)	3339(4)	1027(3)	32(3)
C(110)	−3286(6)	3586(4)	325(3)	35(3)
N(21)	1787(5)	3345(3)	3665(3)	36(2)
C(22)	3104(7)	3797(4)	3882(4)	41(3)
O(22)	3457(4)	4408(3)	3429(2)	41(2)
C(23)	4122(7)	3617(4)	4613(4)	52(3)
C(24)	3771(7)	3036(4)	5150(4)	52(3)
C(25)	1917(7)	2046(4)	5537(4)	46(3)
C(251)	2881(7)	1874(5)	6407(4)	77(4)
C(26)	546(7)	1690(4)	5285(4)	48(3)
C(27)	−380(7)	1846(3)	4490(3)	38(3)
C(271)	−1849(7)	1475(4)	4258(4)	41(3)
C(272)	−2408(8)	684(4)	4545(4)	56(4)
C(273)	−3766(9)	372(5)	4373(5)	72(4)
C(274)	−4602(8)	832(6)	3935(5)	74(4)
C(275)	−4095(8)	1603(5)	3622(5)	69(4)
C(276)	−2713(8)	1924(4)	3779(4)	51(3)
N(28)	60(5)	2381(3)	3950(3)	33(2)
C(29)	1399(7)	2744(3)	4209(3)	35(3)
C(210)	2394(6)	2597(4)	4974(3)	40(3)
C(5)	635(7)	704(5)	2295(4)	96(5)
Cl(51)	474(4)	108(2)	3146(2)	153(2)
Cl(52)	2348(3)	1220(3)	2531(3)	172(2)
Cl(53)	−207(4)	−4(2)	1172(2)	195(3)
C(6)	1626(6)	7341(4)	2224(4)	69(4)
Cl(61)	19(3)	7220(2)	2271(2)	106(2)
Cl(62)	1600(3)	7481(2)	1109(2)	106(1)
Cl(63)	2836(3)	8298(2)	3110(2)	151(2)
C(7)	−3890(7)	4795(4)	2935(4)	64(4)
Cl(71)	−2889(3)	5408(2)	2385(2)	105(2)
Cl(72)	−4548(3)	3608(2)	2348(2)	121(2)
Cl(73)	−2879(2)	4893(2)	4107(1)	106(1)
2·2$CHCl_3$				
Ru(1)	187(1)	313(1)	707(1)	32(1)
O(11)	1772(7)	967(8)	639(5)	41(3)
O(12)	1402(7)	329(8)	−756(5)	40(3)
C(11)	2046(11)	803(12)	−75(9)	44(5)
C(12)	3238(12)	1246(18)	−112(11)	71(7)
N(1)	895(8)	−1399(9)	1032(6)	36(4)
C(2)	1237(10)	−1491(12)	1906(8)	39(5)
O(2)	1065(7)	−560(8)	2341(5)	46(3)
C(3)	1806(11)	−2602(12)	2287(8)	43(5)
C(4)	1956(11)	−3502(14)	1774(8)	49(5)
C(5)	1595(11)	−4372(10)	247(8)	38(5)
C(51)	2140(16)	−5606(14)	540(10)	66(7)
C(6)	1124(11)	−4144(12)	−629(9)	46(5)
C(7)	627(11)	−3035(12)	−950(8)	41(5)
C(71)	136(11)	−2867(13)	−1898(8)	44(5)
C(72)	−484(12)	−3846(14)	−2387(9)	57(6)
C(73)	−851(14)	−3746(18)	−3267(11)	72(7)
C(74)	−634(17)	−2698(23)	−3716(11)	93(9)
C(75)	−24(16)	−1802(15)	−3230(10)	69(7)
C(76)	362(13)	−1850(13)	−2332(9)	53(6)
N(8)	557(8)	−2081(9)	−382(6)	33(3)
C(9)	1001(10)	−2330(12)	496(8)	37(5)
C(10)	1518(10)	−3443(12)	829(8)	40(5)
C	1028(15)	1575(17)	7051(12)	136(15)
Cl(1)	1149(12)	3062(12)	7480(9)	293(7)
Cl(2)	609(8)	1545(12)	5911(6)	258(8)
Cl(3)	2366(5)	871(6)	7405(4)	119(3)
3b·1.5$C_6H_4Cl_2$·0.5CH_3OH				
Ru(1)	1242(1)	3259(1)	3428(1)	52(1)
Ru(2)	−45(1)	1746(1)	3077(1)	46(1)
O	2538(7)	4755(7)	3654(7)	62(3)
N(11)	−845(8)	2023(7)	2214(7)	46(3)
C(12)	−504(8)	2996(7)	2343(7)	51(5)
O(12)	321(7)	3682(7)	2918(6)	54(3)
C(13)	−1085(11)	3280(11)	1881(9)	54(5)
C(14)	−1973(11)	2587(9)	1304(10)	74(6)
C(15)	−3171(10)	824(10)	448(10)	64(5)
C(151)	−3783(13)	1054(13)	−119(12)	90(7)

(continued)

Table 2 (*continued*)

Atom	x	y	z	U_{eq}
C(16)	−3406(10)	−137(11)	310(10)	67(5)
C(17)	−2790(8)	−315(6)	800(8)	56(5)
C(171)	−3025(9)	−1362(7)	634(7)	50(4)
C(172)	−2295(7)	−1589(8)	814(7)	70(5)
C(173)	−2546(10)	−2560(10)	672(8)	97(7)
C(174)	−3527(11)	−3306(7)	350(9)	127(10)
C(175)	−4258(8)	−3080(8)	170(8)	120(9)
C(176)	−4007(8)	−2108(10)	312(8)	91(7)
N(18)	−1951(8)	384(8)	1439(7)	44(3)
C(19)	−1691(8)	1332(8)	1579(8)	48(4)
C(110)	−2288(9)	1579(9)	1110(9)	53(5)
N(21)	534(9)	1251(7)	2158(7)	47(3)
C(22)	1111(10)	1913(7)	1841(8)	47(4)
O(22)	1425(8)	2842(7)	2228(6)	60(3)
C(23)	1354(12)	1543(11)	1079(8)	65(5)
C(24)	1144(11)	598(10)	719(9)	59(5)
C(25)	549(11)	−1005(8)	876(8)	51(4)
C(251)	830(14)	−1419(13)	114(11)	87(6)
C(26)	173(13)	−1506(10)	1395(8)	74(6)
C(27)	−101(12)	−1115(8)	2080(7)	58(5)
C(271)	−405(10)	−1624(9)	2698(7)	70(6)
C(272)	−875(11)	−2649(9)	2418(7)	113(9)
C(273)	−1120(11)	−3102(7)	3002(10)	153(12)
C(274)	−896(11)	−2531(11)	3867(9)	125(10)
C(275)	−427(9)	−1506(11)	4147(6)	99(8)
C(276)	−181(8)	−1053(7)	3563(8)	63(5)
N(28)	25(9)	−197(7)	2334(7)	48(3)
C(29)	402(10)	330(8)	1854(7)	43(4)
C(210)	679(11)	−41(8)	1132(7)	43(4)
N(31)	961(8)	3769(8)	4596(7)	48(4)
C(32)	1630(10)	4676(9)	5228(9)	59(5)
O(32)	2492(9)	5093(9)	5222(7)	82(4)
C(33)	1277(12)	5104(12)	5873(10)	74(6)
C(34)	341(10)	4656(9)	5896(9)	61(5)
C(35)	−1286(9)	3193(10)	5239(9)	55(5)
C(351)	−1675(14)	3635(12)	5871(11)	88(7)
C(36)	−1881(10)	2247(10)	4622(9)	63(5)
C(37)	−1486(8)	1842(6)	4063(8)	54(5)
C(371)	−2101(8)	762(6)	3478(6)	49(4)
C(372)	−1714(7)	147(9)	3476(6)	62(5)
C(373)	−2304(10)	−868(8)	3018(8)	83(6)
C(374)	−3280(10)	−1269(6)	2562(7)	77(6)
C(375)	−3667(6)	−655(10)	2564(7)	92(7)
C(376)	−3077(9)	360(9)	3022(8)	79(6)
N(38)	−558(7)	2314(7)	4025(7)	45(3)
C(39)	27(8)	3252(8)	4606(7)	44(4)
C(310)	−291(10)	3702(9)	5252(8)	56(5)
N(41)	2160(8)	2806(8)	3928(8)	53(4)
C(42)	1660(7)	2036(9)	4172(8)	50(5)
O(42)	715(6)	1525(7)	3971(6)	51(3)
C(43)	2194(10)	722(11)	4651(10)	64(5)
C(44)	3180(10)	2169(12)	4824(11)	85(6)
C(45)	4732(9)	3302(12)	4604(12)	75(6)
C(451)	5376(14)	3086(15)	5099(14)	110(8)
C(46)	5118(12)	3959(13)	4208(11)	87(7)
C(47)	4505(9)	4193(10)	3787(10)	70(6)
C(471)	4878(12)	4807(10)	3257(10)	85(7)
C(472)	5878(11)	5484(12)	3507(9)	115(9)
C(473)	6257(9)	6039(9)	3019(12)	134(11)
C(474)	5634(15)	5917(10)	2281(11)	131(11)
C(475)	4634(13)	5241(12)	2031(8)	108(8)
C(476)	4255(8)	4686(9)	2519(10)	104(8)

(*continued*)

Table 2 (*continued*)

Atom	x	y	z	U_{eq}
N(48)	3532(9)	3814(9)	3673(8)	66(4)
C(49)	3128(8)	3150(12)	4036(11)	67(5)
C(410)	3707(9)	2874(11)	4489(10)	62(5)
Cl(11)	7395(11)	4605(11)	544(9)	159(6)
Cl(12)	6195(11)	2818(9)	−1257(12)	187(7)
C(11′)	7494(18)	4611(19)	−489(13)	68(10)
C(12′)	6984(16)	3860(14)	−1305(17)	96(13)
C(13′)	7213(17)	4034(15)	−2029(12)	67(10)
C(14′)	7952(18)	4960(18)	−1936(13)	60(9)
C(15′)	8462(15)	5711(13)	−1120(16)	82(12)
C(16′)	8233(17)	5536(16)	−396(12)	77(11)
Cl(21)	4901(9)	810(12)	3007(12)	176(7)
Cl(22)	3197(10)	1032(12)	2283(10)	171(7)
C(21′)	5079(22)	1706(15)	2545(15)	74(11)
C(22′)	4331(15)	1851(16)	2216(16)	96(13)
C(23′)	4538(16)	2596(18)	1899(15)	76(11)
C(24′)	5494(19)	3197(14)	1911(14)	41(8)
C(25′)	6242(13)	3052(18)	2240(17)	163(22)
C(26′)	6035(18)	2307(21)	2557(17)	93(13)
Cl(31)	111(13)	5755(11)	1628(11)	168(6)
Cl(32)	1491(14)	6922(14)	669(11)	187(7)
C(31′)	1618(37)	7391(34)	1687(19)	160(9)
C(33′)	942(25)	6959(22)	2097(31)	160(9)
C(35′)	1090(29)	7462(35)	2963(32)	160(9)
C(32′)	1913(36)	8395(34)	3419(19)	160(9)
C(34′)	2589(24)	8827(22)	3009(31)	160(9)
C(36′)	2441(29)	8324(35)	2143(31)	160(9)
O(4′)	4858(17)	9172(16)	4105(14)	73(7)
C(4′)	5691(29)	9746(28)	4732(25)	89(12)

[a] Equivalent isotropic temperature factors U_{eq} are defined as one third of the trace of the orthogonalised U_{ij} tensor.

diruthenium(II,III) species containing 2,6-substituted pyridinato ligands, e.g. $[Ru_2Cl(hp)_4(Hhp)]$ (Hhp = pyridin-2-one), $[Ru_2Cl(chp)_4]$ (Hchp = 6-chloropyridin-2-one), $[Ru_2Cl(PhNpy)_4]$ (PhNHpy = 2-anilinopyridine), $[Ru_2Cl(OAc)_2(PhNpy)_2(PhNHpy)]$ [10] and $[Ru_2(chp)_4(py)](BF_4)$ [11]. It is apparent that the presence of an axially coordinated Cl^- ion in diruthenium(II,III) complexes favours the adoption of the polar arrangement of ligands irrespective of whether there is potential steric

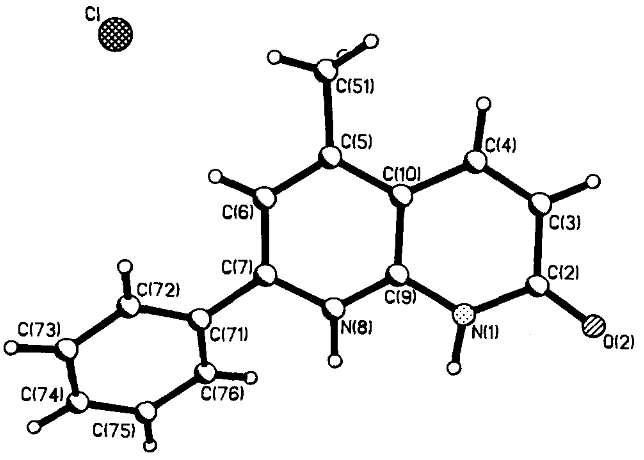


Fig. 1. Structure of $[H_2mphonp]Cl$.

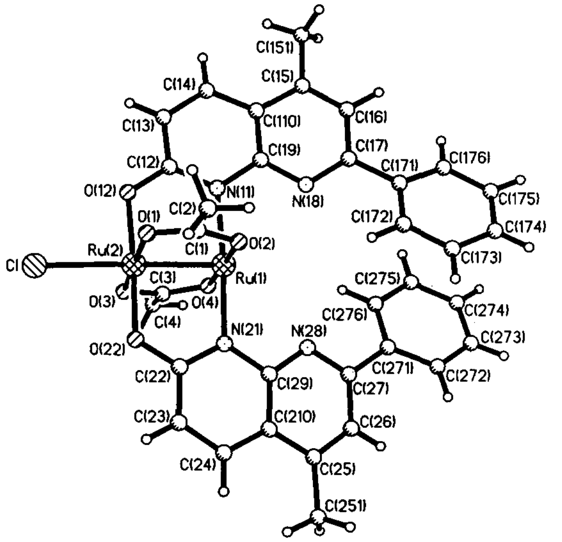


Fig. 2. Molecular structure of $[Ru_2Cl(mphonp)_2(OAc)_2]$ (1). Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.285(1), Ru(2)–Cl 2.458(2), Ru(1)–N(11) 2.064(4), Ru(1)–N(21) 2.065(5), Ru(1)–O(2) 2.022(4), Ru(1)–O(4) 2.019(4), Ru(2)–O(12) 2.005(4), Ru(2)–O(22) 2.012(4), Ru(2)–O(1) 2.035(4), Ru(2)–O(3) 2.025(4); N(1)–Ru(1)–Ru(2) 87.8(1), N(21)–Ru(1)–Ru(2) 88.3(1), N(11)–Ru(1)–N(21) 176.1(2), O(12)–Ru(2)–Ru(1) 91.6(1), O(22)–Ru(2)–Ru(1) 91.2(1), O(12)–Ru(2)–O(22) 177.2(2), Cl–Ru(2)–Ru(1) 178.4(1), Cl–Ru(2)–O(12) 88.9(1), Cl–Ru(2)–O(22) 88.3(1).

crowding of ligand substituents. As in the case of $[Ru_2Cl(mhp)_2(OAc)_2]$ (prepared by reaction of $[Ru_2Cl(OAc)_4]$ with Hmhp in methanol at reflux [9]) only two of the four bridging acetate ligands have been replaced in **1**, despite the employment of a 1:4 molar ratio of $[Ru_2Cl(OAc)_4]$ and Hmphonp. It seems reasonable to assume that no degree of ligand twisting would allow four $mphonp^-$ ligands to all point the same way in a potential species of the type $[Ru_2Cl(mphonp)_4]$. The Ru–Ru distance of 2.285(1) Å in **1** falls within the typical range (2.248(1)–2.308(1) Å) for diruthenium(II,III) complexes [12]. A marked shortening of the Ru–Cl bond in **1** (2.458(2) Å) is observed in comparison to Ru_2^{5+} species containing axial ligands at both ends of the metal–metal bond (2.517(2)–2.587(5) Å [12]). Similar Ru–Cl distances are exhibited by $[Ru_2Cl(mhp)_2(OAc)_2]$ (2.419(5) Å [9]), $[Ru_2Cl(PhNpy)_4]$ (2.437(7) Å [10]) and $[Ru_2Cl(chp)_4]$ (2.443(2) Å [10]). The bridging ligands in **1** display a relatively small degree of twist as evidenced by the following torsion angles: O(1)–Ru(2)–Ru(1)–O(2) 5.6°, O(3)–Ru(2)–Ru(1)–O(4) 4.4°, O(12)–Ru(2)–Ru(1)–N(11) 6.8°, O(22)–Ru(2)–Ru(1)–N(21) 6.8°.

The first quadruply bridged diruthenium(II,II) complex to be isolated and characterised was $[Ru_2(mhp)_4]$, prepared by Garner and co-workers in 1981 in low yield (8%) by reaction of $[Ru_2Cl(OAc)_4]$ with Na(mhp) in CH_3OH at room temperature under a nitrogen atmosphere [13]. Cotton and co-workers have subsequently reported that the reaction of $[Ru_2Cl(OAc)_4]$ with the lithium or sodium salt of an anionic bridging ligand generally leads to the formation of an intractable palette of products [10c]. The presence of the bulky substituent in Hmphonp would, however, be expected to both slow the rate of further substitution of the bridging acetate ligands and markedly reduce the number of potential isomeric products. Our study of the heterogeneous reaction of **1** with Na(mphonp) has now confirmed these predictions. A FAB mass spectrum of the reaction precipitate taken after 6 h contained *m/z* peaks at 1144 $[Ru_2(mphonp)_4H]^+$ and 792 $[Ru_2(mphonp)_2(OAc)_2H]^+$, indicating that both reduction of the Ru_2^{5+} core to Ru_2^{4+} and further substitution of the acetate ligands had occurred. Although separation of the products by column chromatography proved to be unsuccessful, fractional crystallisation did allow the isolation of $[Ru_2(mphonp)_2(OAc)_2]$ (**2**) and $[Ru_2(mphonp)_4]$ (**3a**).

The structure of the centrosymmetric dimeric complex **2** is depicted in Fig. 3. Interestingly the coordination mode of the $mphonp^-$ ligands changes from O,N to N,N′ on going from **1** to **2**. The *trans*-sited bridging naphthyridine ligands now point in opposite directions, i.e. N1 and N8a are in *trans* position to one another. It may be assumed that the alternative ligand orientation (N1 *trans* to N1a, N8 *trans* to N8a) would lead to intolerably short contacts between adjacent phenyl substituents. The N,N′ coordination mode was also observed for the four bridging ligands in $[Ru_2(monp)_4]$ [6]. **2** exhibits an Ru–Ru distance of 2.268(2) Å typical for Ru_2^{4+} cores (2.235(1)–2.28(2) Å [12]).

The fully substituted dinuclear complex $[Ru_2(mphonp)_4]$ (**3a**) may be obtained in high yield (89%) by refluxing $[Ru_2Cl(OAc)_4]$ (**1**) and Hmphonp in an NaOMe/HOMe solution for 36 h. **3a** was characterised by FAB mass spec-

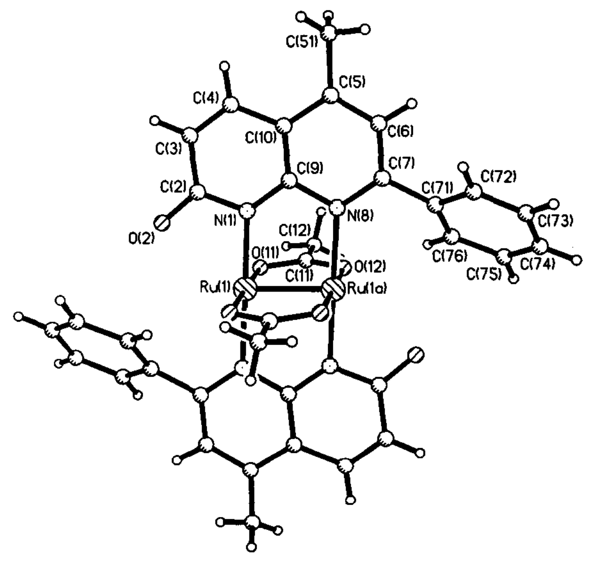


Fig. 3. Molecular structure of $[Ru_2(mphonp)_2(OAc)_2]$ (2). Selected bond distances (Å) and angles (°): Ru(1)–Ru(1a) 2.268(2), Ru(1)–N(1) 2.058(10), Ru(1)–O(11) 2.065(9), Ru(1)–O(12a) 2.055(9), Ru(1)–N(8a) 2.128(9); N(1)–Ru(1)–Ru(1a) 86.4(3), N(8a)–Ru(1)–Ru(1a) 94.1(3), O(11)–Ru(1)–Ru(1a) 90.0(2), O(12a)–Ru(1)–Ru(1a) 89.4(2), N(1)–Ru(1)–O(11) 89.9(4), N(1)–Ru(1)–N(8a) 179.3(4), N(1)–Ru(1)–O(12a) 90.6(4), O(11)–Ru(1)–N(8a) 90.7(4), O(11)–Ru(1)–O(12a) 179.2(3), N(8a)–Ru(1)–O(12a) 88.9(4).

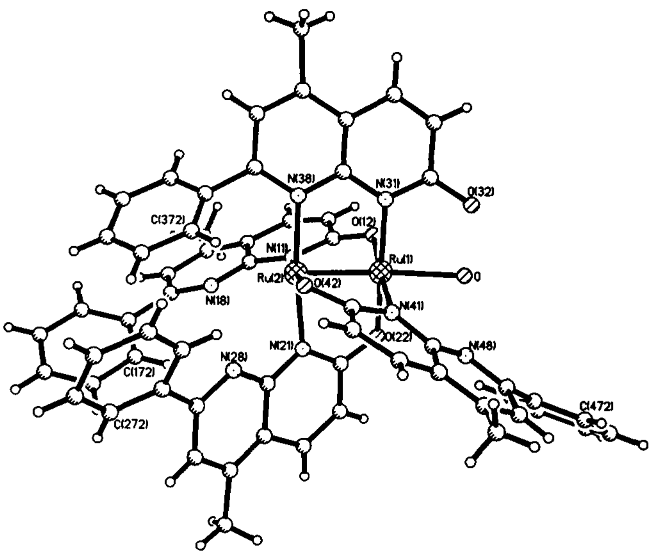


Fig. 4. Molecular structure of $[Ru_2(mphonp)_4(H_2O)]$ (**3b**). Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.238(2), Ru(1)–O 2.271(9), Ru(1)–O(12) 2.06(1), Ru(1)–O(22) 2.05(1), Ru(1)–N(31) 2.11(1), Ru(1)–N(41) 2.09(1), Ru(2)–N(11) 2.08(1), Ru(2)–N(21) 2.06(1), Ru(2)–N(38) 2.07(1), Ru(2)–O(42) 2.02(1); Ru(2)–Ru(1)–O 174.8(3), O(12)–Ru(1)–Ru(2) 90.1(3), O(22)–Ru(1)–Ru(2) 90.8(3), N(31)–Ru(1)–Ru(2) 90.4(3), N(41)–Ru(1)–Ru(2) 89.1(3), O(12)–Ru(1)–O(22) 87.5(4), O(12)–Ru(1)–N(31) 85.2(4), O(12)–Ru(1)–N(41) 179.0(4), O(22)–Ru(1)–N(31) 172.6(5), O(22)–Ru(1)–N(41) 92.0(5), N(31)–Ru(1)–N(41) 95.3(5), N(11)–Ru(2)–Ru(1) 89.2(3), N(21)–Ru(2)–Ru(1) 86.8(3), N(38)–Ru(2)–Ru(1) 96.3(3), O(42)–Ru(2)–Ru(1) 90.2(3), N(11)–Ru(2)–N(21) 91.8(5), N(11)–Ru(2)–N(38) 88.6(5), N(11)–Ru(2)–O(42) 176.7(4), N(21)–Ru(2)–N(38) 177.0(4), N(21)–Ru(2)–O(42) 91.4(4), N(38)–Ru(2)–O(42) 88.1(4).

trometry and elemental analysis. As discussed in Section 1, steric crowding of *cis*-sited 2- and 7-substituents would be expected to prevent the formation of a uniquely N,N′ coordinated dinuclear complex such as $[Ru_2(monp)_4]$. Attempts to grow single crystals of **3a** suitable for X-ray structural analysis were unsuccessful for a large number of solvents tried. However it did prove possible to obtain a few single crystals of the water adduct $[Ru_2(mphonp)_4(H_2O)]$ (**3b**) by slow vapour diffusion of hexane into a dichlorobenzene solution of **3a**. In retrospect it must be assumed that the dichlorobenzene solvent employed was slightly wet. The molecular structure of **3b** is depicted in Fig. 4. Whereas three of the substituted naphthyridine ligands exhibit the N,O coordination mode, the fourth bridging anion retains the N,N′ coordination mode observed in complex **2**. Two of the *cis*-sited N,O ligands in **3b** point in the same direction as the N,N′ ligand, leading to a pronounced degree of steric crowding between 7-phenyl substituents, which is alleviated by extreme ligand twisting. This may be gauged from the following torsion angles: O(12)–Ru(1)–Ru(2)–N(11) 18.8°, O(22)–Ru(1)–Ru(2)–N(21) 20.9°, N(31)–Ru(1)–Ru(2)–N(38) 15.8°, N(41)–Ru(1)–Ru(2)–O(42) 22.8°.

Tetracarboxylate complexes of the type $Ru_2(O_2CR)_4$ are known to bind O-donor ligands such as THF or acetone only weakly [14]. Indeed such ligands can readily be removed by heating in vacuum. It should, however, be noted that axial coordination of Ru(1) in the polar complex **3b** is stabilized by the formation of an O–H···O hydrogen bond of length 2.57 Å to the adjacent 2-substituted O(32) of the N,N′ coordinated bridging ligand. Of interest is also the observation that the Ru–Ru distance in **3b** (2.238(2) Å) is significantly shorter than that in **2** (2.268(2) Å) or in $[Ru_2(monp)_4]$ (2.258(2) Å [6]), despite the presence of an axial water molecule.

Clear structural evidence for the $\delta^2\pi^4\delta^2\pi^{*2}\delta^{*2}$ electronic configuration in the diruthenium(II,II) complexes **2**, **3a** and **3b** is provided by the fact that their Ru–Ru bond lengths are essentially the same as those for diruthenium(II,III) cations $[Ru_2(O_2CR)_4]^+$ for which the $\delta^2\pi^4\delta^2\delta^{2*}$ configuration is certain. The temperature dependence of the magnetic susceptibilities of the complexes $[Ru_2(mhp)_4]$, $[Ru_2(chp)_4]$ and $[Ru_2(bhp)_4]$ (Hbhp = 6-bromopyridin-2-one) is also in accordance with the latter configuration [15]. The magnetic moments μ_{eff} of these compounds lie in the range 2.2–2.8 BM at 293 K. $[Ru_2(monp)_4]$ displays a similar magnetic behaviour with a μ_{eff} value of 2.51 BM at room temperature [6].

Taken together with the structure of $[Ru_2(monp)_4]$, the present findings present strong evidence for an electronic preference of the Ru_2^{4+} core for the N,N′ rather than the N,O coordination by naphthyridin-2-ones. It seems reasonable to conclude that the former binding mode will enhance the interaction between the occupied δ^* orbital of the Ru_2^{4+} core and the π^* molecular orbitals of the aromatic bridging anions. The adoption of the N,O coordination by three of the four $mphonp^-$ ligands in **3b** is clearly the result of steric factors which prevent the formation of a uniquely N,N′ coordinated dinuclear complex $[Ru_2(mphonp)_4]$.

4. Supplementary material

Full details of the crystal structure analyses may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggerstein-Leopoldshafen, by citing the deposition number CSD-58811, the authors and the journal reference.

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References

[1] (a) L. Sacconi, C. Mealli and D. Gatteschi, *Inorg. Chem., 13* (1974) 1985; (b) W.R. Tikkanen, E. Binamira-Soriaga, W.C. Kaska and P.C. Ford, *Inorg. Chem., 23* (1984) 141.

[2] (a) E.L. Enwall and K. Emerson, *Acta Crystallogr. Sect. B, 35* (1979) 2562; (b) G.W. Bushnell, K.R. Dixon and M.A. Kahn, *Can. J. Chem., 56* (1978) 450; (c) J.M. Epstein, J.C. Dewan, D.L. Kepert and A.H.

White, *J. Chem. Soc., Dalton Trans.,* (1974) 1949; (d) A. Clearfield and P. Singh, *J. Chem. Soc., Chem. Commun.,* (1970) 389.

[3] (a) W.R. Tikkanen, E. Binamira-Soriaga, W.C. Kaska and P.C. Ford, *Inorg. Chem., 22* (1983) 1147; (b) J.L. Bear, L.K. Chau, M.Y. Chavan, F. Lefoulon, R.P. Thummel and K.M. Kadish, *Inorg. Chem., 25* (1986) 1516; (c) R.P. Thummel, F. Lefoulon, D. Williamson and M. Chavan, *Inorg. Chem., 25* (1986) 1675.

[4] (a) E. Binamira-Soriaga, N.L. Keder and W.C. Kaska, *Inorg. Chem., 29* (1990) 3167; (b) J.-P. Collin, A. Jouaiti, J.-P. Sauvage, W.C. Kaska, M.A. McLoughlin, N.L. Keder, W.T.A. Haarison and G.D. Stucky, *Inorg. Chem., 29* (1990) 2238.

[5] (a) R.H. Clayton, M.H. Chisholm, J.C. Huffman and E.B. Lobkovsky, *Angew. Chem., 103* (1990) 893; (b) R.H. Cayton, M.H. Chisholm, J.C. Huffman and E.B. LLobkovsky, *J. Am. Chem. Soc., 113* (1991) 8709.

[6] W.S. Sheldrick and M. Mintert, *Inorg. Chim. Acta, 219* (1994) 23.

[7] (a) R.A. Henry and P.R. Hammond, *J. Heterocycl. Chem., 14* (1977) 1109; (b) E.V. Brown, *J. Org. Chem., 30* (1969) 1607.

[8] G.M. Sheldrick, *SHELXL-93,* a program for structure refinement, Göttingen, Germany, 1993

[9] A.R. Chakravarty, F.A. Cotton and D.A. Tocher, *Inorg. Chem., 24* (1985) 2857.

[10] (a) A.R. Chakravarty, F.A. Cotton and D.A. Tocher, *Inorg.Chem., 24* (1985) 172; (b) *24* (1985) 1263; (c) A.R. Chakravarty and F.A. Cotton, *Inorg. Chim. Acta, 105* (1985) 19.

[11] F.A. Cotton, Y. Kim and T. Ren, *Inorg. Chem., 31* (1992) 2602.

[12] F.A. Cotton and R.A. Walton, *Multiple Bonds Between Metal Atoms,* Clarendon, Oxford, 2nd edn., 1993, pp. 400–415.

[13] M. Berry, C.D. Garner, I.H. Hillier, A.A. MacDowell and W. Clegg, *Inorg. Chim. Acta, 53* (1981) L61.

[14] A.J. Lindsay, G. Wilkinson, M. Motevalli and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.,* (1987) 2723.

[15] F.A. Cotton, T. Ren and J.L. Eglin, *J. Am. Chem. Soc., 112* (1990) 3439.