Mixed-ligand Complexes of Ruthenium-(III) and -(II) with Ethylenediaminetetraacetate and Bidentate Phosphines and Arsines[†]

Mirza M. Taqui Khan,* Krishnan Venkatasubramanian, Zahida Shirin and Mohan M. Bhadbhade
Central Salt & Marine Chemicals Research Institute, Bhavnagar 364 002, India

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Interaction of $K[Ru(Hedta)Cl]\cdot 2H_2O$ and $[Ru(Hedta)(H_2O)]$ (edta = ethylenediaminetetraacetate) with bis(diphenylphosphino)methane (dppm) in water–ethanol mixture produces [Ru(Hedta)(dppm)] and $[Ru(H_2edta)(dppm)]$. The complex [Ru(Hedta)(dppm)] on reduction with molecular hydrogen in dimethyl sulfoxide (dmso) gave $[Ru(H_2edta)(dppm)]\cdot dmso\cdot H_2O$. Reaction of K[Ru(Hedta)Cl] and $[Ru(H_2edta)(H_2O)]$ with $NPr^i(PPh_2)_2$, 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(diphenylarsino)ethane (dpae) gave mononuclear complexes of general formulae [Ru(Hedta)(L–L)] and $[Ru(H_2edta)(L–L)]$ which present a combination of hard and soft donor atoms in the co-ordination sphere. All these complexes were characterized by physicochemical studies. The X-ray crystallographic study of $[Ru(H_2edta)(dppm)]\cdot dmso\cdot H_2O$ reveals that the co-ordination sites of the distorted ruthenium(II) octahedron are occupied by the tetradentate edta and dppm which binds as a bidentate moiety with a four-membered chelate ring having each phosphorus *trans* to the nitrogen atoms of the ethylenediamine collar. Hydrogens of the two protonated free carboxyl groups of the edta moiety and the water molecule take part in an extensive hydrogen-bonding network.

The chemistry of ruthenium phosphine/arsine and diphosphine/diarsine complexes is quite extensive and has been studied in detail by many workers.[1-4] Aminopolycarboxylic acid complexes of ruthenium have also been studied.[5-8] However, complexes containing both phosphine/arsine and aminopolycarboxylic acid ligands and combinations of soft and hard donor ligands have been relatively less explored.

In view of the complex-forming ability of Ru^{III} and Ru^{II} with hard N, O and soft P donor atoms exhibited in catalytic reactions,[9] it is of considerable interest and importance to investigate the mixed-ligand complexes of Ru^{III} and Ru^{II} with ethylenediaminetetraacetic acid (H_4edta) and chelating phosphines and arsines. These complexes can exhibit interesting structural chemistry and reactivity patterns.

The present investigation deals with the synthesis of mixed-ligand ruthenium(III) complexes [Ru(Hedta)(L–L)] formed by the interaction of $K[Ru(Hedta)Cl]\cdot 2H_2O$ with $Ph_2PCH_2PPh_2$ (dppm), $NPr^i(PPh_2)_2$, $Ph_2PCH_2CH_2PPh_2$ (dppe) and $Ph_2AsCH_2CH_2AsPh_2$ (dpae). The complex [Ru(Hedta)(dppm)] undergoes reduction to the corresponding ruthenium(II) complex by molecular hydrogen in dimethyl sulfoxide (dmso) under ambient conditions to form $[Ru(H_2edta)(dppm)]\cdot dmso\cdot H_2O$ which was characterized by crystal structure determination. In order to understand the geometry of the mixed-ligand complexes, we have also prepared the ruthenium(II) analogues and investigated their proton NMR spectra.

Experimental

Physical Measurements.—Microanalysis of the elements carbon, hydrogen, nitrogen and phosphorus were conducted by the Australian Mineral Development Laboratories (AMDEL), Australia. Conductivity measurements were made at 30 °C on a Digisun digital conductivity meter which was calibrated with 0.1 mol dm^{-3} KCl before use. Magnetic susceptibility were measured by the Evans method.[10] Infrared spectra (4000–200 cm^{-1}) were recorded on a Specord M80 Carl-Zeiss Jena spectrometer in KBr, $^{31}P-\{^1H\}$ NMR spectra on a JEOL FX 100 NMR spectrometer using 85% phosphoric acid as external standard. The proton NMR spectra of the complexes were recorded on a Bruker AMX-400 MHz spectrometer at the Indian Institute of Science, Bangalore, using $SiMe_4$ as external standard.

Cyclic voltammograms were recorded on a PARC model 174A polarographic analyser, model 175 universal programmer and model 303 SMDE/HMDE three-electrode cell assembly. A glassy carbon electrode was used as working electrode. The auxiliary electrode was a platinum wire and an Ag–AgCl electrode was used as reference electrode. A high-precision x-y recorder was used to record the *i vs. E* plots at a fixed potential range. Solutions of the complexes in methanol were employed with tetrabutylammonium perchlorate used as supporting electrolyte.

Materials and Methods.—The compound $RuCl_3\cdot 3H_2O$ was purchased from Johnson Matthey. The ligands dppm, dppe and dpae were obtained from Strem Chemical; $NPr^i(PPh_2)_2$ was a generous gift from Professor S. S. Krishnamurthy, Indian Institute of Science, Bangalore. The salt Na_2H_2edta was of A.R. grade (BDH). Solvents used were of analytical grade and all the reactions were carried out under an argon atmosphere.

Synthesis of Complexes.—The complex $K[Ru(Hedta)Cl]\cdot 2H_2O$ was prepared by the literature method;[7] $[Ru(H_2edta)(H_2O)]$ was prepared by removal of chloride ion from the above chloro complex with Ag_2CO_3 and then reducing it with platinum black–H_2 gas.

Ruthenium(III) *complexes.* [Ru(Hedta)(dppm)] **1**. An aqueous solution of $K[Ru(Hedta)Cl]\cdot 2H_2O$ (0.5 g, 1 mmol) was added to a refluxing ethanolic solution of dppm (0.38 g, 1 mmol) under argon. The initially red solution become orange after being refluxed for about 2–3 h and upon cooling a yellow precipitate formed. The precipitate was isolated by filtration, washed several times with warm water and diethyl ether and dried under vacuum. Yield 84% (0.65 g) (Found: C, 55.2; H, 4.60; N, 2.90; P, 7.6. Calc. for $C_{35}H_{35}N_2O_8P_2Ru$: C, 54.3; H, 4.50; N, 3.60; P, 8.0%).

[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

[Ru(Hedta){NPr^i(PPh$_2$)$_2$}] **2**. The reaction of K[Ru(Hedta)Cl]·2H_2O (0.2 g, 0.4 mmol) with NPr^i(PPh$_2$)$_2$ in water–ethanol (1:1) was carried out as for complex **1**. Yield: 61% (0.2 g) (Found: C, 54.40; H, 4.90; N, 5.15; P, 7.30. Calc. for $C_{37}H_{41}N_3O_8P_2Ru$: C, 54.35; H, 5.00; N, 5.15; P, 7.6%).

[Ru(Hedta)(dppe)] **3**. Reaction of K[Ru(Hedta)Cl] (0.2 g, 0.4 mmol) with dppe (0.16 g, 0.4 mmol) was carried out as for complex **1**. Yield: 81% (0.26 g) (Found: C, 54.20; H, 4.70; N, 3.10; P, 7.60. Calc. for $C_{36}H_{37}N_2O_8P_2Ru$: C, 54.80; H, 4.70; N, 3.55; P, 7.85%).

[Ru(Hedta)(dpae)] **4**. The reaction of K[Ru(Hedta)Cl] (0.2 g, 0.4 mmol) with dpae (0.19 g, 0.4 mmol) was carried out as for complex **1**. Yield: 75% (0.25 g) (Found: C, 48.90; H, 4.10; N, 3.00. Calc. for $C_{36}H_{37}As_2N_2O_8Ru$: C, 49.25; H, 4.20; N, 3.20%).

Ruthenium(II) *complexes.* [Ru(H_2edta)(dppm)]·dmso·H_2O **5** (*hydrogenation method*). Complex **1** (0.5 g) was dissolved in dmso (20 cm^3) and molecular hydrogen was bubbled through the solution for about 10–12 h at ambient pressure and temperature. The colour of the solution changed from orange-yellow to yellow. The complex crystallized as yellow crystals from the solution of dmso. Yield: 62% (0.34 g) (Found: C, 51.10; H, 5.15; N, 3.20; P, 7.15. Calc. for $C_{37}H_{44}N_2O_{10}P_2RuS$: C, 50.95; H, 5.05; N, 3.20; P, 7.10%).

Alternate method. An aqueous solution of [Ru(Hedta)(H_2O)] (0.2 g) containing Platinum Black (10 mg) was placed in a Schlenk tube fitted with a side arm. The solution was saturated with argon then hydrogen gas was bubbled through it to reduce Ru^{III} to Ru^{II}. A deep yellow solution was filtered under argon after 0.5 h. An alcoholic solution of dppm (0.188 g) was added to the filtrate without interrupting the flow of argon. The solution immediately turned orange and then bright yellow. The solution was treated as above yielding [Ru(H_2edta)(dppm)] **5a** as yellow crystals. Yield: 67% (0.25 g) (Found: C, 54.10; H, 4.65; N, 3.65. Calc. for $C_{35}H_{36}N_2O_8P_2Ru$: C, 54.20; H, 4.65; N, 3.60%).

The complexes [Ru(H_2edta){NPr^i(PPh$_2$)$_2$}] **6**, [Ru(H_2edta)(dppe)] **7** and [Ru(H_2edta)(dpae)] **8** were synthesised by the same method. The elemental analyses of complexes **5a** and **6**–**8** gave identical results to those of the ruthenium(III) analogue.

Structural Determination of Complex **5**.—Complex **5** crystallizes as yellow plates from a solution of dimethyl sulfoxide. A crystal of dimensions 0.09 × 0.08 × 0.11 mm was used both for data collection and preliminary studies. Accurate cell dimensions were obtained using 25 arbitrarily chosen high-order reflections. Extinction conditions, hkl, $h + k = 2n + 1$, define the space group as $C1$ or $C\bar{1}$. Intensity statistics, however, indicated it to be centrosymmetric $C\bar{1}$, which was confirmed by the successful solution and refinement.

Crystal data. $M = 871$, triclinic, space group $C\bar{1}$, $a = 23.836(1)$, $b = 16.578(1)$, $c = 9.780(1)$ Å, $\alpha = 87.859(10)$, $\beta = 98.019(9)$, $\gamma = 91.335(6)^\circ$, $U = 3823$ Å^3, $Z = 4$, $D_c = 1.821$ g cm^{-3}, $\mu = 76.1$ cm^{-1}, $F(000) = 1792$.

Intensity data (h, $\pm k$, $\pm l$) were collected at 295 K on an Enraf-Nonius CAD-4 diffractometer in ω–2θ scan mode with graphite-monochromatized Cu-Kα (λ = 1.5418 Å) radiation. The crystal stability and orientation during data collection were monitored using three control reflections each. Intensities were collected for the Lorentz and polarization effects. An empirical absorption correction was then applied using three strong reflections (near $\chi = 90^\circ$) by the ψ-scan method.[11] Of the 4807 reflections collected in the 2θ range 4–130°, 4146 had $I > 3\sigma(I)$ and were considered as observed.

The structure was solved by the heavy-atom method; a difference map phased on the ruthenium atom gave the positions of a few non-hydrogen atoms. Difference maps, alternated with least-squares refinement, led to the location of all the non-hydrogen atoms. All the hydrogen atoms were located after anisotropic refinement of non-hydrogen atoms. Full-matrix least-squares refinements of all the non-hydrogens refined anisotropically and the hydrogens held fixed with a unit weighting scheme employing the Dunitz–Seiler factor,[12] after correcting for extinction, yielded a final R value of 0.031 (R' = 0.032). In the final cycle of refinement the shift-to-error ratios for non-hydrogen atoms were less than 0.01:1 showing that the refinement fully converged. The difference map at this stage was devoid of any major features. All the computations were carried out using the SDP package.[13]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The ruthenium(III) complexes **1**–**4** were synthesised by the interaction of K[Ru(Hedta)Cl]·2H_2O with dppm, NPr^i(PPh$_2$)$_2$, dppe and dpae in ethanol–water mixtures. The ruthenium(II) complexes **5**–**8** were prepared with [Ru^{II}(H_2edta)(H_2O)] as the starting material and the same ligands as those for complexes **1**–**4**. Complex **5** was also synthesised by the interaction of molecular hydrogen in dmso. The conductivity values of all these complexes show non-electrolyte nature. The magnetic moments (μ_{eff}) for complexes **1**–**4** as determined by the Evans[10] method show values in the range 2.01–1.85 which is the region expected for a low-spin d^5 system.[8,14,15] Complexes **5**–**8** are diamagnetic.

The infrared spectra of all the complexes display peaks due to the presence of both the primary ligand edta and secondary phosphines/arsine ligands (Table 1). The absorption in the carbonyl region is important in establishing the presence and absence of unionized co-ordinated and free ionized carboxylate groups.[16] Complexes **1**–**8** show an intense band around 1720–1732 cm^{-1} due to the presence of an unionized (protonated) free carboxylate group of edta.[7,8,16] A strong broad band at 1580–1640 cm^{-1} shows the presence of co-ordinated carboxylate groups. The band due to a free ionized carboxylato group falls in the range 1560–1580 cm^{-1}, but for these complexes this band merges into that due to the co-ordinated carboxylate group due to the broad nature of the peak. Complexes **1**–**3** and **5**–**7** show two medium-intensity bands in the ranges 495–525 and 535–550 cm^{-1} which are assigned to M–P stretching.[4,17] This indicates the *cis* disposition of two phosphine groups in these complexes. Complexes **4** and **8** shows two bands, around 405 and 425 cm^{-1} assigned to *cis* M–As bonds.[4,16]

The ^{31}P NMR spectra of the ruthenium(III) complexes give broad peaks due to the presence of paramagnetic Ru^{III}; the spectra of the ruthenium(II) complexes are however sharp. The ^{31}P-{^{1}H} NMR spectrum of complex **1** shows a broad singlet at δ 13.44 indicating that the two phosphorus groups of the dppm ligand are magnetically equivalent ($\Delta = \delta_{co\text{-}ord} - \delta_{free\ ligand} = 36.1$ ppm, $\delta_{free\ dppm} = -22.6$). The spectrum of complex **2** shows a singlet at δ 4.83 ($\Delta = 36.1$ ppm, $\delta_{free\ phosphine}$ 48.8). Complex **3** shows a singlet at δ 69.99. Both the phosphorus groups of dppe are magnetically equivalent ($\Delta = 83.1$ ppm, $\delta_{free\ dppe}$ −13.08).

The ^{31}P NMR spectrum of complex **1** in dmso gave a singlet at δ 13.44. On bubbling H_2 gas through this solution for 4 h the spectrum showed two doublets centred at δ 28.4 and −27.5 with J(P–P) = 50 Hz. The first doublet is due to the co-ordinated phosphorus atom and the second is due to free phosphorus atoms of dppm. On keeping the solution for a long time the spectrum contained a sharp singlet at δ 12.77 owing to closure of the dppm ring (complex **5**). The slight downfield shift from its ruthenium(III) analogue may be due to the solvent effect ($\Delta = 35.41$ ppm, $\delta_{free\ dppm} = -22.64$). The ^{31}P-{^{1}H} NMR spectra of complexes **6** and **7** are identical to those of their ruthenium(III) analogues, but with a sharp peak due to the diamagnetic nature of the complexes.

It is worth commenting on the chemical shifts of the diphosphine ligands in their complexes. In the case of dppm and NPr^i(PPh$_2$)$_2$, where they form four-membered rings, Δ is ~36 whereas in the case of dppe which forms a five-membered ring Δ = 83 ppm. This indicates that the five-membered ring is more

Table 1 Infrared spectral data (cm^{-1}) for mixed-ligand complexes of Ru^{II} and Ru^{III}

Complex	$\nu(CO_2H)$	$\nu(CO_2{-}M)$	$\nu(CO_2)$	$\nu(M{-}P)$, $\nu(M{-}As)$
1 $[Ru^{III}(Hedta)(dppm)]$	1735	1610	1585	550, 510
2 $[Ru^{III}(Hedta)\{NPr^i(PPh_2)_2\}]$	1730	1600s	—	525, 560
3 $[Ru^{III}(Hedta)(dppe)]$	1712	1620	1575	535, 560
4 $[Ru^{III}(Hedta)(dpae)]$	1730	1650	1585	410, 435
5 $[Ru^{II}(H_2edta)(dppm)]\cdot dmso\cdot H_2O$	1725	1605	1585	510, 545
5a $[Ru^{II}(H_2edta)(dppm)]$	1725	1605s	1580	510, 545
6 $[Ru^{II}(H_2edta)\{NPr^i(PPh_2)_2\}]$	1735	1595s	—	530, 555
7 $[Ru^{II}(H_2edta)(dppe)]$	1720	1640s	1580	545, 495
8 $[Ru^{II}(H_2edta)(dpae)]$	1725	1640	1595	405, 425

Table 2 Proton NMR spectral data (relative to $SiMe_4$) of some Ru^{II}edta mixed-ligand complexes

Complex	
5a $[Ru(H_2edta)(dppm)]$	3.16, 3.2, 3.82, 3.96, 4.05 (edta) 4.82 (t), 7.45–7.97 (br m) (dppm) edta: dppm = 1:2
6 $[Ru(H_2edta)\{NPr^i(PPh_2)_2\}]$	0.85 (d), 0.899 (d), 3.5 (m), 7.5–8.5 (br m) $[NPr^i(PPh_2)_2]$ 3.1, 3.12, 3.8, 3.84, 3.9, 4.1 (edta) edta: $NPr^i(PPh_2)_2$ = 1:3
7 $[Ru(H_2edta)(dppe)]$	2.7, 3.1, 3.5, 3.8, 4.13 (edta) 4.15, 4.25, 7.5–8.4 (dppe) edta: dppe = 1:2
8 $[Ru(H_2edta)(dpae)]$	3.17, 3.2, 3.5, 3.8, 3.9 (edta) 4.3, 7.5–8.2 (dpae) edta: dpae = 1:2

stable and the phosphorus atoms in complex **5** are more shielded than in the four-membered ring complexes *i.e.* **1**, **2** and **5**, **5a**, **6**.[17–20]

Proton NMR spectral data for the ruthenium(II) complexes **5**–**8** are given in Table 2. In all cases, and within the limitations stated in the Table, the spectra confirm the ratio between the protons of edta and those of the ligand, in agreement with the formulations. The complex $[Ru(H_2edta)(dppm)]$ **5a** shows resonances for the co-ordinated dppm ligand, a multiplet at δ 7.45–7.97 and a triplet at 4.82 [J(P–H) = 10 Hz] due to the phenyl and methylene protons. The methylene triplet at δ 4.82 is due to the splitting by two equivalent phosphine atoms.

The spectrum of complex **6** shows two doublets at δ 0.899 and 0.851 [J(H–H) = 6 Hz] due to CH_3 protons, a multiplet at δ 3.5 due to the CH proton and a multiplet at δ 8.5–7.5 due to phenyl protons of the ligand $NPr^i(PPh_2)_2$. The free ligand shows a doublet at δ 1.12 [J(H–H) = 6 Hz] due to the CH_3 group, a multiplet at δ 3.5 due to CH and a multiplet at δ 7.2–7.7 due to phenyl protons. After chelation the methyl protons do not seem equivalent, possibly due to the change in geometry of the two isopropyl methyl groups.

Complex **7** show a multiplet at δ 7.5–8.4 due to phenyl protons and two multiplets at δ 4.25 and 4.15 due to methylene protons. The methylene protons in the chelated ligand are not equivalent because in the five-membered ring such protons are expected to be above and below the plane containing the metal ion and two phosphorus atoms. The spectrum of the complex $[Ru(H_2edta)(dpae)]$ **8** shows a similar pattern to that of $[Ru(H_2edta)(dppe)]$ **7**. The only difference is that the methylene protons appears as two singlets since there is no splitting by the arsine group.

The integration of the phenyl and methylene protons in these complexes is consistent with the proposed structures. All these complexes show peaks due to the co-ordinated edta group.

The cyclic voltammograms of the ruthenium(II) complexes **1**–**4** in methanol display a reversible one-electron couple assigned to Ru^{III}–Ru^{II} at +0.67, +0.71, +0.69 and +0.60 V, respectively, whereas for the chloro complex [Ru(Hedta)Cl] the value for the corresponding couple in water is −0.24 V *vs.* saturated calomel electrode (SCE).[21,22] The positive shift (0.84–0.96 V) in $E_{\frac{1}{2}}$ values for this couple in complexes **1**–**4** when compared to that of chloro edta complexes can be accounted by the presence of the π-acceptor phosphine/arsine ligands. These complexes and their corresponding reduced forms **5**–**8** also showed a one-electron irreversible reduction step corresponding to the Ru^{II}–Ru^{I} couple at −0.70, −0.56, −0.72 and −0.58 V, respectively.

Structure of $[Ru(H_2edta)(dppm)]\cdot dmso\cdot H_2O$ **5**.—Table 3 gives the final positional parameters for non-hydrogen atoms and Tables 4 and 5 the bond lengths and angles in the molecule. Fig. 1 shows a perspective view of complex **5** with the atom numbering scheme. The solvated complex occurs as a DL-stereoisomeric pair, related by a centre of symmetry in $C\bar{1}$. The edta occurs as a tetradentate moiety which has a non-crystallographic approximate two-fold symmetry, dppm forms a strained four-membered chelate ring with each phosphorus *trans* to the nitrogen atom of the ethylenediamine collar of edta. The co-ordination octahedron of Ru is distorted as can be seen from the deviation of the bond angles from 90° (or 180° for *trans* atoms).

The ligand dppm can act as a mono-, bi-dentate or bridging bidentate. In the complex [Ru(dppm-*P*)(dppm-*P*,*P'*)(η^5-C_5H_5)] it is both a mono- and bi-dentate.[23] A number of complexes in which dppm occurs as a bridging bidentate ligand have been reported recently.[24–26] In one of these cases, namely [Ru(dppm-*P*)(dppm-*P*,*P'*)(η^5-C_5H_5)], the angle P–Ru–P in the four-membered ring is 74.3°. In *trans*-$[RuCl_2(dppm)_2]$,[27] the P–Ru–P angle is 71.4°. These angles compare well with the P–Ru–P angle of 70.74(3)° observed in the present structure. In cases of dppm acting as a bidentate ligand co-ordinated to a single metal ion, contraction of the tetrahedral angle of the methylene carbon connecting the two phosphorus atoms occurs. The angle P(21)–C(34)–P(35) in complex **5** is 91.5(1)° which agrees well with that of 91.6° in [Ru(dppm-*P*)(dppm-*P*,*P'*)(η^5-C_5H_5)].[23] The steric constraints of the four-membered ring are also felt at the phosphorus atoms. The angles Ru–P(21)–C(34) and Ru–P(35)–C(34) are 94.4(2) and 94.4(2)°, respectively. The corresponding values in [Ru(dppm-*P*)(dppm-*P*,*P'*)(η^5-C_5H_5)] are 97.5(3) and 96.3(3)°,[23] respectively. When dppm is chelated in the bidentate mode to a single metal site the P · · · P distance shortens (2.637 Å in **5**). This can be compared with the value of 2.670 Å in [Ru(dppm-*P*)(dppm-*P*,*P'*)(η^5-C_5H_5)].[23] In the complexes of dppe, however, a five-membered chelate ring is formed and the P–M–P angle opens to 79–84° as found in *trans*-$[TcCl_2(dppe)_2]$ and *trans*-$[TcCl_2(dppe)_2]NO_3\cdot HNO_3$.[28]

Weakliem and Hoard[29] have classified the five-membered chelate rings of edta into three groups, E, R and G, depending upon the disposition of the rings. Ring E is formed from the ethylenediamine backbone; R is approximately perpendicular to and G almost parallel to the N–M–N plane. In the present

Table 3 Positional parameters of non-hydrogen atoms and their estimated standard deviations for complex **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.836 21(1)	−0.001 22(1)	0.221 08(2)	C(22)	0.747 5(1)	0.160 3(2)	0.274 0(3)
S(48)	1.012 78(5)	−0.417 57(7)	0.154 7(2)	C(23)	0.714 8(2)	0.177 1(3)	0.373 8(4)
P(21)	0.818 46(3)	0.117 89(4)	0.315 17(7)	C(24)	0.660 6(2)	0.208 1(3)	0.336 6(5)
P(35)	0.802 94(3)	−0.027 25(4)	0.425 02(7)	C(25)	0.639 3(2)	0.220 2(2)	0.199 9(5)
O(13)	0.724 2(1)	0.031 2(2)	−0.132 8(3)	C(26)	0.672 2(2)	0.203 8(3)	0.009 7(4)
O(14)	0.762 38(8)	−0.004 1(1)	−0.079 7(2)	C(27)	0.726 1(2)	0.174 1(2)	0.136 8(4)
O(15)	0.990 7(1)	0.162 3(2)	−0.040 9(3)	C(28)	0.865 4(1)	0.207 1(2)	0.326 6(3)
O(16)	0.931 7(1)	0.090 0(2)	−0.186 7(3)	C(29)	0.846 7(2)	0.284 0(2)	0.284 0(4)
O(17)	0.994 1(1)	−0.089 4(2)	0.352 4(3)	C(30)	0.884 4(2)	0.348 9(2)	0.289 9(5)
O(18)	0.919 59(9)	−0.009 6(1)	0.318 8(2)	C(31)	0.940 5(2)	0.338 2(3)	0.341 8(5)
O(19)	0.766 0(1)	−0.310 7(2)	0.141 4(4)	C(32)	0.959 5(2)	0.262 3(3)	0.386 0(5)
O(20)	0.856 2(1)	−0.290 9(2)	0.111 6(4)	C(33)	0.922 3(2)	0.196 9(2)	0.378 2(4)
O(51)	0.970 4(2)	−0.485 8(2)	0.160 4(6)	C(36)	0.727 6(1)	−0.041 2(2)	0.436 2(3)
O(52)	0.862 9(1)	−0.438 7(2)	0.050 1(4)	C(37)	0.707 7(2)	−0.046 5(3)	0.563 1(4)
N(1)	0.871 2(1)	0.031 6(2)	0.026 3(3)	C(38)	0.649 5(2)	−0.051 9(4)	0.568 1(5)
N(4)	0.853 6(1)	−0.124 3(2)	0.166 8(3)	C(39)	0.612 3(2)	−0.053 1(3)	0.448 1(6)
C(2)	0.898 3(1)	−0.044 0(2)	−0.007 3(3)	C(40)	0.631 3(2)	−0.047 9(3)	0.320 6(5)
C(3)	0.862 7(2)	−0.117 8(2)	0.017 9(3)	C(41)	0.689 7(1)	−0.042 4(2)	0.314 8(4)
C(5)	0.822 3(2)	0.053 3(2)	−0.077 0(4)	C(42)	0.838 5(1)	−0.100 8(2)	0.550 3(3)
C(6)	0.765 4(1)	0.023 4(2)	−0.041 5(3)	C(43)	0.894 9(2)	−0.087 4(2)	0.605 7(3)
C(7)	0.913 3(1)	0.097 3(2)	0.048 5(3)	C(44)	0.923 9(2)	−0.147 2(3)	0.686 7(4)
C(8)	0.949 4(1)	0.119 3(2)	−0.065 4(3)	C(45)	0.897 2(2)	−0.219 7(3)	0.715 0(5)
C(9)	0.906 0(1)	−0.148 2(2)	0.257 6(3)	C(46)	0.841 3(3)	−0.233 2(3)	0.659 0(5)
C(10)	0.942 7(1)	−0.077 1(2)	0.312 0(3)	C(47)	0.812 4(2)	−0.173 7(2)	0.579 7(4)
C(11)	0.805 0(1)	−0.180 1(2)	0.182 2(3)	C(49)	0.989 7(3)	−0.357 5(3)	0.003 7(6)
C(12)	0.807 2(1)	−0.267 4(2)	0.142 3(3)	C(50)	0.994 7(3)	−0.346 2(5)	0.276 6(7)

Table 4 Bond distances (Å)

Ru–P(21)	2.283(8)	C(8)–O(15)	1.204(5)
Ru–P(35)	2.272(7)	C(8)–O(16)	1.310(4)
Ru–O(14)	2.082(2)	N(4)–C(9)	1.481(4)
Ru–O(18)	2.087(3)	C(9)–C(10)	1.519(4)
Ru–N(1)	2.230(3)	C(10)–O(17)	1.253(4)
Ru–N(4)	2.192(3)	C(10)–O(18)	1.268(4)
N(1)–C(2)	1.475(5)	N(4)–C(11)	1.488(5)
C(2)–C(3)	1.504(5)	C(11)–C(12)	1.518(5)
C(3)–N(4)	1.503(4)	C(12)–O(19)	1.203(4)
N(1)–C(5)	1.475(5)	C(12)–O(20)	1.315(5)
C(5)–C(6)	1.514(5)	P–C	1.834(4)[a]
C(6)–O(13)	1.238(4)	C–C	1.382(7)[b]
C(6)–O(14)	1.266(4)	S(48)–O(51)	1.504(5)
N(1)–C(7)	1.466(4)	S(48)–C(49)	1.779(6)
C(7)–C(8)	1.528(5)	S(48)–C(50)	1.813(9)

Numbers in parentheses are estimated standard deviations in the least significant digits. [a] Average value of six P–C distances. [b] Average of 24 C–C bonds in the four benzene rings.

Table 5 Bond angles (°)

P(21)–Ru–P(35)	70.74(3)	N(1)–C(2)–C(3)	111.9(3)
P(21)–Ru–O(14)	96.11(6)	C(2)–C(3)–N(4)	110.2(3)
P(21)–Ru–O(18)	95.53(6)	N(1)–C(5)–C(6)	114.8(3)
P(21)–Ru–N(1)	106.14(7)	C(5)–C(6)–O(13)	116.8(3)
P(21)–Ru–N(4)	170.17(7)	C(5)–C(6)–O(14)	118.8(3)
P(35)–Ru–O(14)	102.33(6)	O(13)–C(6)–O(14)	124.3(2)
P(35)–Ru–O(18)	90.75(7)	N(1)–C(7)–C(8)	118.6(3)
P(35)–Ru–N(1)	176.41(7)	C(7)–C(8)–O(15)	119.8(4)
P(35)–Ru–N(4)	100.01(7)	C(7)–C(8)–O(16)	116.1(3)
O(14)–Ru–O(18)	90.75(7)	O(15)–C(8)–O(16)	124.2(3)
O(14)–Ru–N(1)	79.61(9)	C(3)–N(4)–C(9)	111.5(3)
O(14)–Ru–N(4)	89.02(9)	C(3)–N(4)–C(11)	109.7(2)
O(14)–Ru–O(18)	164.79(9)	C(9)–N(4)–C(11)	112.7(2)
O(18)–Ru–N(1)	87.78(9)	N(4)–C(9)–C(10)	113.7(2)
O(18)–Ru–N(4)	80.99(9)	C(9)–C(10)–O(17)	117.8(3)
N(1)–Ru–N(4)	83.0(1)	C(9)–C(10)–O(18)	118.6(2)
Ru–N(1)–C(2)	103.9(2)	O(17)–C(10)–O(18)	123.5(3)
Ru–N(1)–C(5)	106.3(2)	N(4)–C(11)–C(12)	119.8(3)
Ru–N(1)–C(7)	110.5(2)	C(11)–C(12)–O(19)	120.0(3)
Ru–N(4)–C(3)	105.2(2)	C(11)–C(12)–O(20)	115.9(3)
Ru–N(4)–C(11)	111.5(2)	O(19)–C(12)–O(20)	124.0(3)
Ru–P(21)–C(22)	118.6(1)	Ru–O(14)–C(6)	117.4(2)
Ru–P(21)–C(28)	103.6(1)	Ru–O(18)–C(10)	115.7(2)
Ru–P(21)–C(34)	94.4(2)	P(21)–C(34)–C(35)	91.5(1)
Ru–P(35)–C(34)	94.4(2)	C–P–C	105.7(1)*
Ru–P(35)–C(36)	122.3(2)	P–C–C	120.2(3)*
Ru–P(35)–C(42)	119.9(1)	C–C–C	120.0(5)*
C(2)–N(1)–C(5)	111.2(2)	O(51)–S(48)–C(49)	107.0(3)
C(2)–N(1)–C(7)	110.6(2)	O(51)–S(48)–C(50)	104.9(3)
C(5)–N(1)–C(7)	112.8(2)	C(49)–S(48)–C(50)	96.1(3)

Numbers in parentheses are estimated standard deviations in the least significant digits. * Average value in the dppm ring.

structure ring E takes up a half-chair conformation with atoms C(2) and C(3) deviating from the plane through N(1)–Ru–N(4) by 0.34 and 0.38 Å, respectively. A similar conformation is found for this ring in the structure $K[Ir(H_2edta)Cl_2]$.[30] The torsion angle N(1)–C(2)–C(3)–N(4) has a value of −59.7(3)°, close to those found in other edta complexes.

Considering the co-ordination of the ethylenediamine collar, the Ru–N(1) and Ru–N(4) distances are 2.230(3) and 2.192(3) Å, respectively, significantly longer than the average Ru^{II}–N distance of 2.144 Å in $[Ru(NH_3)_6]I_2$[31] and 2.058(4) and 2.036(4) Å in $[Ru(H_2dmg)_3]Cl_2$ (H_2dmg = dimethylglyoxime).[32] This can be attributed to the *trans* influence of the P atoms of dppm in complex **5**. The Ru–P(21) and Ru–P(35) distances of 2.283(8) and 2.272(7) Å respectively are much shorter than those observed (2.29–2.37 Å) in *trans*-$[RuCl_2(dppm)_2]$.[27] Ruthenium(II)–phosphorus distances typically span the range 2.32–2.44 Å depending on the σ basicity or π acidity of the *trans* ligand.[33,34] In complex **5** the strong σ donation by the N atom of edta is responsible for the greater back donation from the filled d_{xz} and d_{yz} orbitals of the metal ion to the empty 3d orbitals of P, making the Ru–P bond more covalent and thus shorter. Alternatively, N has a net low *trans* influence so Ru–P *trans* to N is expected to be shorter than Ru–P *trans* to P because of σ effects. The Ru–O(14) and Ru–O(18) distances of 2.082(2) and 2.087(3) Å are equal within experimental error and are in the normal range.

The bond lengths and angles in the dimethyl sulfoxide moiety compare well with the reported values.[35–39] Dimethyl sulfoxide is not co-ordinated to the metal but gives stability to

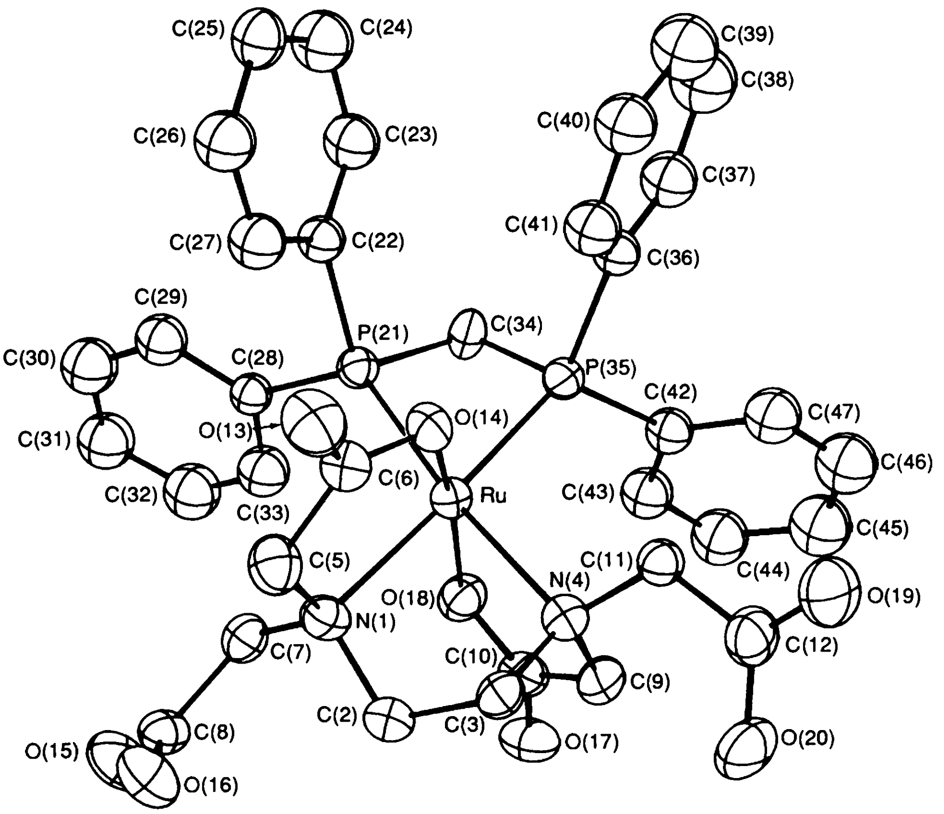

Fig. 1 ORTEP diagram of the $[Ru(H_2edta)(dppm)]$ moiety of complex **5** showing the atom labelling scheme

the structure by its involvement as an acceptor of hydrogen bonding.

A network of hydrogen bonds occurs in the crystal and all the hydrogens available for bonding are utilized. Hydrogen atom H(161), attached to the hydroxyl group O(16) of the free carboxylate arm, is bonded on O(17) of a symmetry-related molecule. The distances O(17)···H(161) (1.636 Å) and O(17)···O(16) (2.562 Å) and the angles subtended at H(161) (155.5°) indicate a strong hydrogen bond. Similarly, H(201), connected to the hydroxyl group O(20) of the free carboxylate arm, is bonded to the water molecule in the same formula unit: O(52)···H(201) and O(52)···O(20) are 1.890 and 2.559 Å, respectively and the angle O(20)–H(201)–O(52) is 146.99°. Of the two water hydrogens, H(521) connects O(52) to O(13) related by C centring, O(13)···H(521) and O(13)···O(52) being 1.639 and 2.736 Å, respectively and the angle subtended at H(521) is 149.63°. Atom H(522) connects O(52) to the oxygen O(51) of the dimethyl sulfoxide, O(51)···H(522) and O(51)···O(52) 1.741 and 2.575 Å, respectively, the angle at H(522) being 166.8°.

In conclusion, the interaction of bidentate phosphine/arsine ligands with $K[Ru(Hedta)Cl]\cdot 2H_2O$ and $[Ru(H_2edta)(H_2O)]$ results in mixed-ligand complexes where the +3 oxidation state of the metal ion is stabilized by the presence of the hard N and O donor atoms of edta and +2 oxidation state is stabilized by the soft P/As donor atoms of the phosphine and arsine ligands.

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