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1,3,4-Thiadiazole-2,5-dithiol Complexes of the Platinum Group Metals; the Molecular Structure of Carbonylbis(1,3,4-thiadiazole-2,5-dithiolato)-bis(triphenylphosphine)ruthenium(II)*

PASQUALE MURA

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Abstract

The precursors $MH_2(CO)(PPh_3)_3$ (M = Ru or Os), $Ru(CO)_3(PPh_3)_2/OsH_2(CO)_2(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$ react with 1,3,4-thiadiazole-2,5-dithiol ($tddtH_2$) in boiling toluene to afford the 1,3,4-thiadiazole-2,5-dithiolato (tddtH) complexes $M(tddtH)_2(CO)(PPh_3)_2$, $M(tddtH)_2(CO)_2(PPh_3)_2$ and $IrH(tddtH)_2(CO)(PPh_3)_2$ respectively. The molecular structure of the ruthenium complex $Ru(tddtH)_2(CO)(PPh_3)_2$ has been determined by X-ray diffraction methods, the crystals are triclinic, space group $P\bar{1}$, $Z = 2$, unit cell dimensions are $a = 13.051(3)$, $b = 16.404(7)$, $c = 16.500(5)$ Å, $\alpha = 119.60(2)$, $\beta = 91.46(2)$, $\gamma = 104.21(3)°$, $V = 2932.0(16)$ Å^3. The structure contains octahedral ruthenium(II) with mono-dentate (S-coordinated) and bi-dentate (N,S-coordinated) tddtH ligands, a carbonyl group and a *trans* pair of triphenylphosphine ligands. The complexes $M(tddtH)_2(CO)(PPh_3)_2$ and the closely related ruthenium 5-methyl-1,3,4-thiadiazole-2-thiolato complex $Ru(mtdt)_2(CO)(PPh_3)_2$ have been shown by ^1H NMR to display dynamic interchange of mono- and bi-dentate thiolate ligands.

Some rhodium(I), palladium(0) and platinum(0) complexes of $tddtH_2$ are tentatively reformulated.

Introduction

The multi-functional N,S-donor ligand 1,3,4-thiadiazole-2,5-dithiol (2,5-dimercapto-1,3,4-thiadiazole), commonly known as bismuthiol(I), complexes with a wide variety of class 'b' metals and has been extensively investigated as an analytical reagent for the detection, separation [2, 3] and gravimetric [4] or spectrophotometric [5–7] determination of numerous metal ions including bismuth [3, 4, 7] palladium [3, 5, 6] platinum [5] and osmium [5].

The free ligand has been shown by X-ray diffraction methods [8] to crystallise as 1,3,4-thiadiazole-2-thiol-5-thione (I) and is thought to exist in solution as a solvent dependent mixture of tautomeric forms (II a $\rightleftharpoons$ b) [9]. However, the brightly coloured metal derivatives tend to be rather insoluble, intractable microcrystalline solids, consequently no diffraction studies have been reported and little is known about their structures. Previous workers in the field have determined molecular stoichiometry [10–15], measured magnetic moments and recorded vibrational or electronic spectra [11–15] but have been unable to reach firm conclusions concerning the tautomeric forms and bonding modes adopted by the multi-dentate 1,3,4-thiadiazole-2,5-dithiolate ligand in the complexes examined. In the absence of reliable evidence some authors have advanced highly speculative structures, including several which make impossible stereochemical demands upon the ligands [10] others have interpreted the low solubility of the complexes as evidence of polymeric structures involving bridging 1,3,4-thiadiazole-2,5-dithiolate ligands [14, 15] and have concluded that, for steric reasons, the ligand is unlikely to bond in chelate mode [11]. The latter conclusion is contrary to the growing weight of structural evidence which clearly establishes the ability of $-\mathrm{N}{=}\overset{|}{\mathrm{C}}{=}\mathrm{S}$ groups to coordinate in chelate fashion [16–18]. Therefore, as part of a more extensive study of N,S-donor ligands we have now prepared a small range of moderately soluble platinum group metal 1,3,4-thiadiazole-2,5-dithiolato complexes containing ancillary triphenylphosphine ligands and have sought to resolve, by a combination of X-ray diffraction methods and variable temperature NMR spectroscopy, some of the uncertainties surrounding the structure and coordination modes of the complexed 1,3,4-thiadiazole-2,5-dithiolate ligand. In order to further our NMR investigations we have also prepared and characterized a ruthenium derivative

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*Complexes of Platinum Metals. Part 27. For Part 26, see ref. [1].

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of the closely related 5-methyl-1,3,4-thiadiazole-2-thiolate ligand.

Experimental

Platinum metal salts were obtained from Johnson Matthey and Co. Ltd., 1,3,4-thiadiazole-2,5-dithiol and 5-methyl-1,3,4-thiadiazole-2-thiol were purchased from the Aldrich Chemical Co. and were used without further purification. Reagent grade solvents dried over molecular sieves were used throughout. All reactions were performed under nitrogen but worked up in air. Platinum metal–triphenylphosphine complexes were prepared by literature methods [19]. Micro-analyses were performed at University College, London, melting points were recorded on a Buchi apparatus using samples sealed in capillaries under nitrogen. Proton NMR spectra were recorded using a Bruker WM 250 (250.13 MHz) spectrometer with TMS as internal reference, ^{31}P NMR spectra were recorded on a Bruker HFX 90 (36.44 MHz) spectrometer using H_3PO_4 as an external referencc. Positive chemical shifts are to low field of the reference. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 983G grating spectrometer.

Carbonylbis(1,3,4-thiadiazole-2,5-dithiolato)bis(triphenylphosphine)ruthenium(II)

A mixture of carbonyl-dihydrido tris(triphenylphosphine)ruthenium (0.30 g, 0.327 mmol) and 1,3,4-thiadiazole-2,5-dithiol (0.147 g, 0.978 mmol) in toluene (120 cm^3) was heated under reflux for 3 h to yield a cloudy orange solution from which an orange precipitate slowly deposited. The precipitate was filtered off and washed with toluene, ethanol and n-hexane, then dried *in vacuo* to yield the required product as orange microcrystals (0.25 g, 80%) M.pt 247–249 °C decomp. (*Anal.* found; C, 51.74; H, 3.23; N, 5.65%. calc. for $C_{41}H_{32}N_4OP_2S_6$-Ru; C, 51.72; H, 3.39; N, 5.88%.

The complex was similarly obtained in 90% yield from carbonylchlorohydridotris(triphenylphosphine)-ruthenium and deposited as orange microcrystals M.pt 249–250 °C decomp. (*Anal.* found; C, 51.90; H, 3.34; N, 6.30%).

Carbonylbis(5-methyl-1,3,4-thiadiazole-2-thiolato)bis(triphenylphosphine)ruthenium(II) 1/1 ethanol solvate

A mixture of carbonyldihydridotris(triphenylphosphine)ruthenium (0.459 g, 0.5 mmol) and 5-methyl-1,3,4-thiadiazole-2-thiol (0.397 g, 3.0 mmol) in toluene (50 cm^3) was heated under reflux for 6 h to afford a yellow solution which slowly darkened to orange. The cooled solution was filtered and evaporated to dryness under reduced pressure. The residue was washed with ethanol (2 × 30 cm^3) and then crystallized from benzene/ethanol. The resulting red crystals were filtered off, washed with ethanol, 60/80 light petroleum and diethyl ether, and then dried *in vacuo* (Yield 0.26 g, 54%) Desolvates 180–183°. M.pt 229–232 °C. (*Anal.* found; C, 56.25; H, 4.30; N, 5.59%. calc. for $C_{45}H_{42}N_4$-$O_2P_2S_4Ru$; C, 56.18; H, 4.40; N, 5.82%).

Dicarbonylbis(1,3,4-thiadiazole-2,5-dithiolato)bis(triphenylphosphine)ruthenium(II)

A mixture of tricarbonylbis(triphenylphosphine)-ruthenium (0.40 g, 0.564 mmol) and 1,3,4-thiadiazole-2,5-dithiol (0.25 g, 1.69 mmol) in toluene (120 cm^3) was heated under reflux for 3 h to form a cloudy yellow solution from which a pale orange precipitate (0.31 g) deposited. The precipitate was filtered off, extracted with chloroform (4 × 20 cm^3), then washed with ethanol and n-hexane and finally dried *in vacuo* to yield the required product as pale orange microcrystals (0.20 g, 36%) M.pt 224–225 °C (*Anal.* found; C, 48.39; H, 3.57; N, 5.59% calc. for $C_{42}H_{32}N_4O_2P_2S_6Ru$; C, 51.5; H, 3.29; N, 5.72%).

Evaporation of the chloroform extracts afforded $Ru(tddtH)_2(CO)(PPh_3)_2$ as orange microcrystals 0.08 g, 15%) spectroscopically identical with an authentic sample.

Conversion of dicarbonylbis(1,3,4-thiadiazole-2,5-dithiolato)bis(triphenylphosphine)ruthenium(II) to carbonylbis(1,3,4-thiadiazole-2,5-dithiolato)bis(triphenylphosphine)ruthenium(II)

A suspension of dicarbonylbis(1,3,4-thiadiazole-2,5-dithiolato)bis(triphenylphosphine)ruthenium (0.10 g) in toluene (50 cm^3) was heated under reflux for 3 h then cooled and filtered. The orange filtrate was reduced to dryness *in vacuo* and the residue was recrystallised from chloroform/n-hexane to yield pale orange microcrystals (0.04 g) of the required product spectroscopically identical with an authentic sample.

The precipitate remaining was identified by spectroscopic methods as unchanged starting material (0.04 g).

Carbonylbis(1,3,4-thiadiazole-2,5-dithiolato)bis(triphenylphosphine)osmium(II)

A suspension of carbonyldihydridotris(triphenylphosphine)osmium (0.25 g, 0.248 mmol) and 1,3,4-thiadiazole-2,5-dithiol (0.112 g 0.746 mmol) in toluene (150 cm^3) was heated under reflux for 4 h to give a yellow solution from which a yellow precipitate slowly deposited. The precipitate was filtered off, washed successively with toluene, ethanol and n-hexane and then dried *in vacuo* to yield the required product as yellow microcrystals (0.24 g, 93%) M.pt 247–248 °C (*Anal.* found; C, 46.80; H, 3.48; N, 5.19% calc. for $C_{41}H_{32}N_4OP_2S_6Os$; C, 47.29; H, 3.10; N, 5.38%).

The complex was similarly obtained in 90% yield from carbonylchlorohydridotris(triphenylphosphine)-osmium and deposited as yellow microcrystals (*Anal.* found, C, 48.00; H, 3.20; N, 5.27%).

Dicarbonyl bis(1,3,4-thiadiazole-2,5-dithiolato)bis(triphenylphosphine)osmium(II)

A suspension of dicarbonyldihydridobis(triphenylphosphine)osmium (0.22 g, 0.285 mmol) and 1,3,4-thiadiazole-2,5-dithiol (0.128 g, 0.852 mmol) in toluene (100 cm^3) was heated under reflux for 6 h to form a cloudy yellow solution from which a yellow precipitate began to form after about 30 min. The precipitate was filtered off and washed successively with toluene, ethanol and n-hexane then dried *in vacuo* to yield the required product as yellow green microcrystals (0.14 g 61%) M.pt 230–231 ℃ (*Anal.* found; C, 46.69; H, 3.09; N, 5.11% calc. for $C_{42}H_{32}N_4O_2P_2S_6Os$; C, 47.18; H, 3.02; N, 5.24%).

Carbonylhydridobis(1,3,4-thiadiazole-2,5,dithiolato)-bis(triphenylphosphine)iridium(III)

A suspension of carbonylchlorobis(triphenylphosphine)iridium (0.39 g, 0.50 mmol) and 1,3,4-thiadiazole-2,5-dithiol (0.225 g, 1.50 mmol) in toluene (100 cm^3) was heated under reflux for 2 h to form a cloudy yellow solution which darkened slowly and deposited an orange precipitate. The precipitate was filtered off and washed successively with toluene, ethanol and n-hexane then dried *in vacuo* to yield the required product as yellow microcrystals (0.44 g, 84%) M.pt 198–200 ℃ with decomp. (*Anal.* found; C, 47.45; H, 3.35; N, 5.30%, calc. for $C_{41}H_{33}N_4OP_2S_6Ir$, C, 47.16; H, 3.19; N, 5.37%).

The complex was similarly obtained as yellow microcrystals (94%) from carbonylhydridotris(triphenylphosphine)iridium.

The reactions of 1,3,4-thiadiazole-2,5-dithiol with mer-trihydridotris(triphenylphosphine)iridium

Mixtures of *mer*-trihydridotris(triphenylphosphine)iridium (0.25 g, 0.255 mmol) and 1,3,4-thiadiazole-2,5-dithiol (0.115 g, 0.765 mmol or 0.04 g, 0.265 mmol) in benzene or toluene (100 cm^3) were heated under reflux for *ca.* 3 h to give yellow or orange solutions which slowly deposited orange yellow precipitates. These very insoluble, intractable products gave analytical and spectroscopic data consistent with their formulation as mixtures.

X-Ray Crystal Structure Determination of Ru(CO)-(C$_2$HN$_2$S$_3$)$_2$(PPh$_3$)$_2$

Orange brown crystals of the complex were obtained by slow evaporation of a chloroform solution. Two crystals were used in data collection. Since the crystals were unstable when removed from the mother liquor, they were sealed in a glass capillary containing a drop of solution.

Crystal Data

$C_{41}H_{32}N_4OP_2RuS_6$, M = 952.13 amu. Triclinic, $a = 13.051(3)$, $b = 16.404(7)$, $c = 16.500(5)$ Å, $\alpha = 119.60(2)$, $\beta = 91.46(2)$, $\gamma = 104.21(3)^\circ$, $V = 2932.0(16)$ Å^3 (by a least-squares procedure from the measured angular positions of 15 reflections), space group $P\bar{1}$, $Z = 2$, $D_c = 1.079$ g cm^{-3} (Because of the instability of the crystals when removed from the mother liquor the experimental density, D_x, could not be measured). Crystal dimensions 0.50 X 0.25 X 0.07 mm and 0.65 X 0.35 X 0.10 mm, $\mu(\text{Mo-K}_\alpha) = 5.47$ cm^{-1}.

Data Collection and Processing

Lattice parameters and intensities were measured with an automatic diffractometer Syntex P21 of the Istituto di Strutturistica Chimica 'G. Giacomello' Research Area of Rome. Three standard reflections showed a steady intensity decrease throughout data collection; the data were corrected both for this decrease and for shape anisotropy of the crystals. The sets of data for the two crystals were put on the same scale using the standard reflections. The data were processed as described in ref. 20, with a value of $p = 0.000137$ as calculated from the variance of the standard reflections [21], and corrected for the Lorenz and polarization effects. Of the 11137 unique data collected 3027 independent reflections with $I > 3\sigma(I)$ were used in the subsequent analysis.

The structure was solved by Patterson and Fourier methods and refined by least squares. The isotropic refinement converged at $R = 0.115$.

In the subsequent least-squares cycles only those atoms not belonging to the phenyl rings were refined anisotropically; phenyl rings were treated as rigid bodies restricted to their idealised geometry (6/mm symmetry), $d(\text{C–C}) = 1.395$ Å, $d(\text{C–H}) = 1.08$Å) with individual isotropic thermal parameters for each carbon atom. Hydrogen atoms were included in the calculation with idealised position and isotropic thermal parameters equal to those of the nearest carbon atoms (the hydrogen atoms bonded to N(2) and to N(4) were not included in the calculation). Convergence was reached at $R = 0.089$ ($R_w = 0.091$).

The final refinement was by full-matrix; the function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with weights of the type $w = 1/[\sigma^2|F_o| + b|F_o|^2]$ with b chosen so as to minimise the dispersion of the values of the minimised function over ranges of reflections ($b = 0.012$). Atomic scattering factors and anomalous dispersion terms were taken from 'International Tables for X-ray Crystallography', (1974).

The calculations were performed on the IBM 370 of CNUCE (Pisa), with the SHELX 76 system of

TABLE I. Positional Parameters for Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses.

	x/a	*y/b*	*z/c*
Non-group atoms			
Ru	0.1255(1)	0.0785(1)	0.2666(1)
S(1)	0.1442(4)	0.2461(4)	0.2982(4)
S(2)	0.2739(5)	0.3779(4)	0.5061(4)
S(3)	0.3828(6)	0.3562(5)	0.6554(4)
S(4)	0.1047(4)	−0.0614(4)	0.2823(4)
S(5)	0.2239(4)	−0.1658(4)	0.3318(5)
S(6)	0.4152(6)	−0.1579(5)	0.4449(7)
P(1)	0.3002(4)	0.0913(4)	0.2233(4)
P(2)	−0.0439(4)	0.0836(4)	0.3188(4)
O(1)	0.0298(12)	−0.0524(13)	0.0607(12)
N(1)	0.2070(12)	0.1972(10)	0.4081(9)
N(2)	0.2569(12)	0.2173(12)	0.4938(13)
N(3)	0.2921(12)	0.0195(12)	0.4081(11)
N(4)	0.3614(12)	−0.0085(11)	0.4435(12)
C(1)	0.0663(17)	−0.0032(17)	0.1361(21)
C(2)	0.2071(13)	0.2747(13)	0.4062(14)
C(3)	0.3094(17)	0.3092(14)	0.5560(14)
C(4)	0.2146(16)	−0.0558(13)	0.3459(13)
C(5)	0.3424(19)	−0.1018(16)	0.4174(17)
Rigid group atoms			
C(111)	0.3513(9)	−0.0133(11)	0.1941(10)
C(112)	0.4505(9)	−0.0041(11)	0.2368(10)
C(113)	0.4808(9)	−0.0877(11)	0.2141(10)
C(114)	0.4119(9)	−0.1806(11)	0.1488(10)
C(115)	0.3128(9)	−0.1898(11)	0.1061(10)
C(116)	0.2824(9)	−0.1062(11)	0.1288(10)
C(121)	0.3121(10)	0.0952(11)	0.1137(10)
C(122)	0.2366(10)	0.1228(11)	0.0791(10)
C(123)	0.2506(10)	0.1342(11)	0.0014(10)
C(124)	0.3401(10)	0.1181(11)	−0.0417(10)
C(125)	0.4155(10)	0.0905(11)	−0.0071(10)
C(126)	0.4015(10)	0.0791(11)	0.0706(10)
C(131)	0.4051(10)	0.2040(8)	0.3082(8)
C(132)	0.4370(10)	0.2815(8)	0.2918(8)
C(133)	0.5150(10)	0.3680(8)	0.3578(8)
C(134)	0.5612(10)	0.3771(8)	0.4402(8)
C(135)	0.5292(10)	0.2997(8)	0.4566(8)
C(136)	0.4512(10)	0.2131(8)	0.3905(8)
C(211)	−0.1409(10)	−0.0342(10)	0.2923(8)
C(212)	−0.2134(10)	−0.0375(10)	0.3521(8)
C(213)	−0.2900(10)	−0.1259(10)	0.3268(8)
C(214)	−0.2942(10)	−0.2110(10)	0.2417(8)
C(215)	−0.2217(10)	−0.2077(10)	0.1819(8)
C(216)	−0.1451(10)	−0.1193(10)	0.2072(8)
C(221)	−0.1311(11)	0.1273(11)	0.2713(8)
C(222)	−0.1149(11)	0.1299(11)	0.1893(8)
C(223)	−0.1849(11)	0.1591(11)	0.1510(8)
C(224)	−0.2711(11)	0.1856(11)	0.1946(8)
C(225)	−0.2873(11)	0.1829(11)	0.2767(8)
C(226)	−0.2173(11)	0.1538(11)	0.3150(8)
C(231)	−0.0225(11)	0.1588(8)	0.4452(9)
C(232)	−0.0211(11)	0.2570(8)	0.4914(9)
C(233)	0.0123(11)	0.3164(8)	0.5893(9)
C(234)	0.0442(11)	0.2777(8)	0.6408(9)
C(235)	0.0427(11)	0.1795(8)	0.5946(9)
C(236)	0.0094(11)	0.1201(8)	0.4967(9)

programs [22], and on the HP21 MX minicomputer of the CNR Research area of Rome using local programs [23].

Final positional parameters for non-hydrogen atoms are given in Table I. The observed and calculated structure factors, the thermal parameters for all non-hydrogen atoms and positional parameters of the hydrogen atoms have been deposited as supplementary data [24].

Results and Discussion

The object of this work was to prepare 1,3,4-thiadiazole-2,5-dithiolato derivatives of the platinum group metals with sufficient solubility in organic solvents to permit solution n.m.r. studies and the growth of crystals suitable for X-ray diffraction. In this way we hoped to obtain unambiguous evidence concerning the bonding modes of the 1,3,4-thiadiazole-2,5-dithiolate (tddtH) anion. To achieve this objective complexes containing ancillary triphenylphosphine ligands were synthesised by heating free 1,3,4-thiadiazole-2,5-dithiol ($tddtH_2$) with suitable platinum metal/triphenylphosphine complexes – notably the hydrido or low oxidation state species $MH_2(CO)(PPh_3)_3$, $MHCl(CO)(PPh_3)_3$ (M = Ru, Os), $Ru(CO)_3(PPh_3)_2$, $OsH_2(CO)_2(PPh_3)_2$, *mer*-$IrH_3(PPh_3)_3$, $IrH(CO)(PPh_3)_3$ and $IrCl(CO)(PPh_3)_2$ in boiling toluene for 3–6 h. The products isolated $M(tddtH)_2(CO)(PPh_3)_2$, $M(tddtH)_2(CO)_2(PPh_3)_2$, (M = Ru or Os) and $IrH(tddtH)_2(CO)(PPh_3)_2$ are all air-stable yellow or orange microcrystalline solids which display very modest solubility in $CHCl_3$, CH_2Cl_2 and Me_2SO and are very sparingly soluble in C_6H_6.

X-ray Diffraction Study; Solid State Structure

Although the complexes are only sparingly soluble it was possible to grow crytals of adequate quality by slow evaporation of chloroform solutions. Therefore, in order to gain direct and unambiguous structural information an X-ray diffraction study of $Ru(tddtH)_2(CO)(PPh_3)_2$ was undertaken. This complex, in which two tddtH ligands share three coordination sites, was chosen with a view to obtaining structural data for mono- and bi-dentate tddtH ligands from a single structure determination.

The crystal structure consists of monomeric units of the complex. Figure 1 shows a perspective view of the molecule indicating the atom numbering scheme employed.

A selection of bond lengths and angles is reported in Table II. The coordination about the ruthenium atom is distorted octahedral with the two triphenylphosphine ligands occupying the axial positions. The four equatorial sites are occupied by (i) the carbonyl group, (ii) a monodentate 1,3,4-thiadiazole-2,5-dithiolate anion bonded through the S(4) atom and

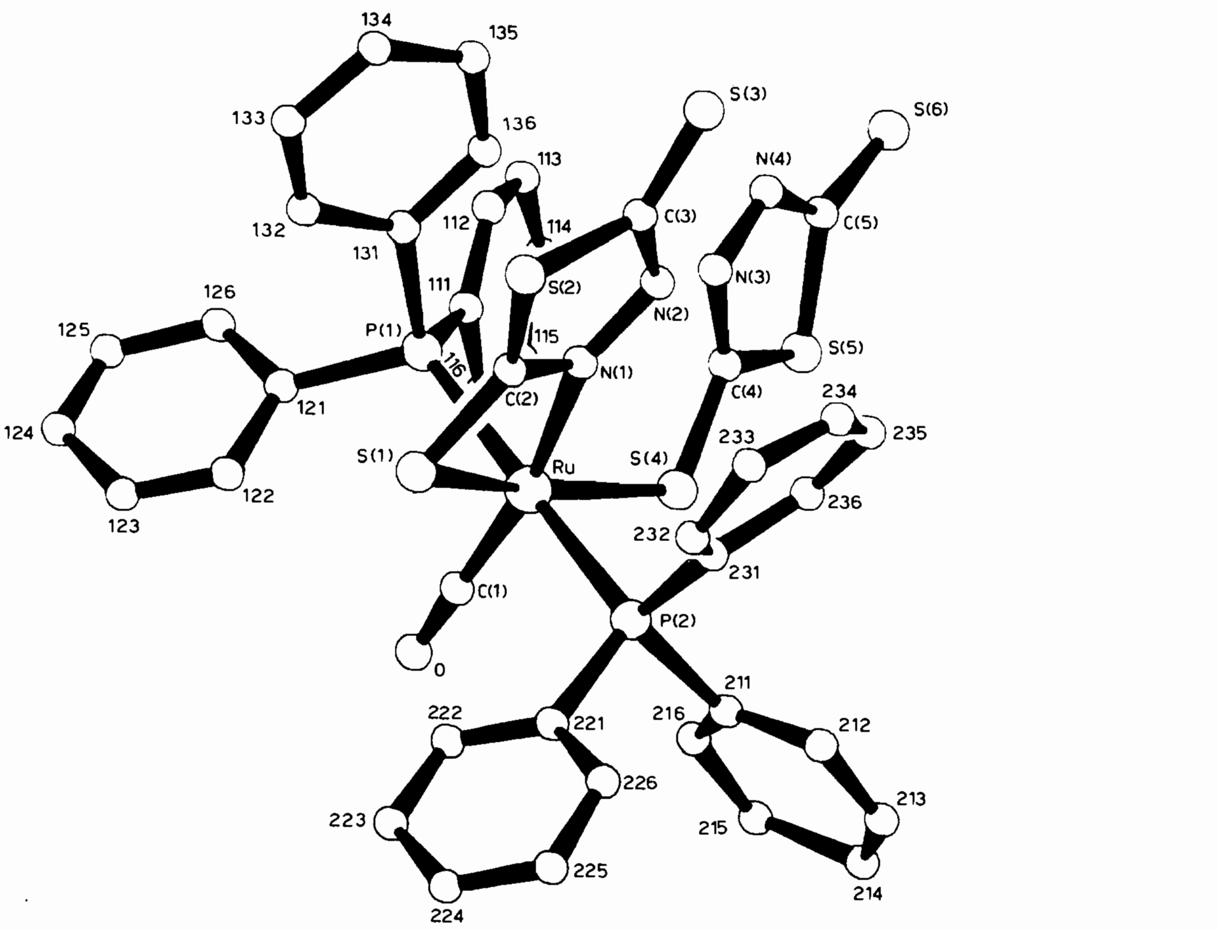


Fig. 1. Perspective view of $Ru(tddtH)_2(CO)(PPh_3)_2$ molecule indicating atom numbering scheme employed.

TABLE II. Selected Bond Distances (Å)[a] and Angles (°).

Ru–P(1)	2.397(5)	S(1)–Ru–S(4)	163.9(2)
Ru–P(2)	2.399(6)	P(1)–Ru–P(2)	174.2(2)
Ru–S(1)	2.478(5)	N(1)–Ru–C(1)	167.1(6)
Ru–S(4)	2.385(5)	S(1)–Ru–N(1)	64.8(4)
Ru–N(1)	2.18(1)	S(1)–Ru–C(1)	103.6(6)
Ru–C(1)	1.89(3)	S(4)–Ru–N(1)	101.3(4)
S(1)–C(2)	1.73(2)	S(4)–Ru–C(1)	91.0(6)
S(2)–C(2)	1.67(2)	Ru–C(1)–O	178(2)
S(2)–C(3)	1.82(2)	Ru–S(1)–C(2)	80.2(6)
S(3)–C(3)	1.58(2)	Ru–N(1)–C(2)	103(1)
S(4)–C(4)	1.71(2)	Ru–S(4)–C(4)	114(6)
S(5)–C(4)	1.74(2)	S(1)–C(2)–N(1)	112(1)
S(5)–C(5)	1.77(2)	S(1)–C(2)–S(2)	136(1)
S(6)–C(5)	1.67(2)	C(2)–S(2)–C(3)	91(9)
O–C(1)	1.10(2)	S(2)–C(3)–S(3)	125(1)
N(1)–N(2)	1.39(2)	S(2)–C(3)–N(2)	104( )
N(1)–C(2)	1.29(2)	S(3)–C(3)–N(2)	131(2)
N(2)–C(3)	1.31(2)	C(3)–N(2)–N(1)	117(2)
N(3)–N(4)	1.35(2)	N(2)–N(1)–C(2)	114(1)
N(3)–C(4)	1.30(2)	N(1)–C(2)–S(2)	113(1)
N(4)–C(5)	1.32(2)	S(4)–C(4)–N(3)	130(1)
		S(4)–C(4)–S(5)	117(1)
		C(4)–S(5)–C(5)	90(1)
		S(5)–C(5)–S(6)	123(1)
		S(6)–C(5)–N(4)	131(2)
		S(5)–C(5)–N(4)	106(1)
		C(5)–N(4)–N(3)	120(2)
		N(4)–N(3)–C(4)	111(2)
		N(3)–C(4)–S(5)	113(1)

[a] Non bonded distance N(2)–H------N(3) 3.00(2).

(iii) a bidentate 1,3,4-thiadiazole-2,5-dithiolate anion chelated through the S(1) and N(1) atoms. The Ru–P distances, 2.397(5) and 2.399(6) Å are similar to those found for *trans* triphenylphosphine ligands in related structures [25–28]. The P(1)–Ru–P(2) angles (66.6(2) and 67.7(2)°) have previously been octahedron is more evident in the small S(1)–Ru–N(1) angle (64.8(4)°) imposed by the narrow bite chelate ligand. Comparable included S–Ru–N angles (66.6(2) and 67.7(2)°) have previously been reported for the bis(pyridine-2-thiolato) chelate $Ru(PyS)_2(PPh_3)_2$ [16]. The Ru–N(1) distance

TABLE III. Infrared Data.[a]

Complex	ν(M–H)	ν(CO)	ν(N–H)	Thioamide[b] Band II	Thioamide[b] Band III
$Ru(tddtH)_2(CO)(PPh_3)_2$	–	1944	2925/2865	1260/1244	1062/1053
$Ru(tddtH)_2(CO)_2(PPh_3)_2$	–	2043/1955	2923/2867	1260	1050
$Os(tddtH)_2(CO)(PPh_3)_2$	–	1928	2928/2860	1260/1243	1062/1055
$Os(tddtH)_2(CO)_2(PPh_3)_2$	–	2035/1971	2938/2883	1268	1050
$IrH(tddtH)_2(CO)(PPh_3)_2$	2160	2037	2928/2868	1265	1051

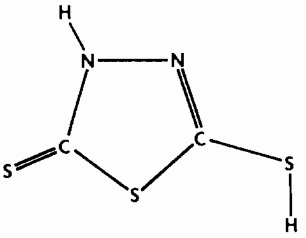
[a] All data in cm^{-1}. [b] Thioamide band I (*ca.* 1480 cm^{-1}) and thioamide band IV (*ca.* 750 cm^{-1}) masked by triphenylphosphine absorptions at *ca.* 1475 and *ca.* 740 cm^{-1} respectively (see text).

TABLE IV. ^1H and $^{31}P\{^1H\}$ N.m.r. Data.[a]

Complex	Temp (K)	δ(NH) ppm	δ(P) ppm
$Ru(tddtH)_2(CO)(PPh_3)_2$	323	11.8	38.0
	296	11.9	
	223	11.9 and 13.1	
$Ru(tddtH)_2(CO)_2(PPh_3)_2$	296	14.1 (broad)[b]	26.9[b]
$Os(tddtH)_2(CO)(PPh_3)_2$	323	11.8	10.4
	296	12.0	
	218	12.0 and 13.1	
$Os(tddtH)_2(CO)_2(PPh_3)_2$	296	13.8(broad)[b]	–5.2[b]
$IrH(tddtH)_2(CO)(PPh_3)_2$[c]	296	13.8 and 13.9[b]	–0.2[b]

[a] In $CDCl_3$ solution unless otherwise indicated. [b] In d_6 DMSO solution. [c] ^1H n.mr., δ(Ir–H) –12.4(t), ^2J(P–H) 12 Hz.

(2.18(1) Å) is similar to those found in related four-membered chelate rings (2.048–2.242 Å) [16, 27, 28]. The Ru–S(1) distance (2.478(5) Å) is significantly longer than the Ru–S(4) distance (2.385(5) Å). The larger value of the Ru–S(1) bond length probably reflects strain resulting from the closure of the four-membered chelate ring. Long Ru–S bonds (2.434(2) and 2.437(2) Å) are also a feature of the chelate pyridine-2-thiolate ligands in $Ru(PyS)_2(PPh_3)_2$ [16]. The overall geometry of the mono- and bi-dentate 1,3,4-thiadiazole-2,5-dithiolate ligands clearly establish that, like the parent molecule [8], both exist in the thiadiazole-2-thiol-5-thione tautomeric form (I). In the mono-dentate tddtH ligand the C_5–N_4–N_3 angle (120(2)°) is significantly larger than the N(4)–N(3)–C(4) angle (111(2)°) thus indicating that the residual proton is situated on N(4) rather than N(3) [29–31]. Finally the short N(2)·····N(3) interligand contact, 3.00(2) Å is consistent with the presence of intramolecular hydrogen bonds N(2)–H·····N(3).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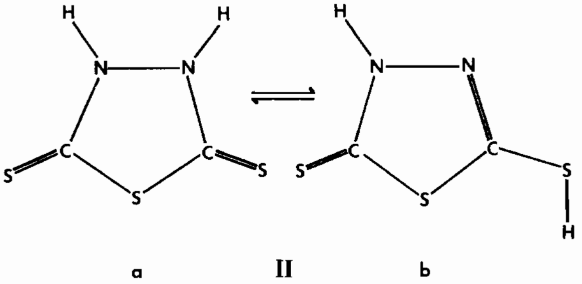


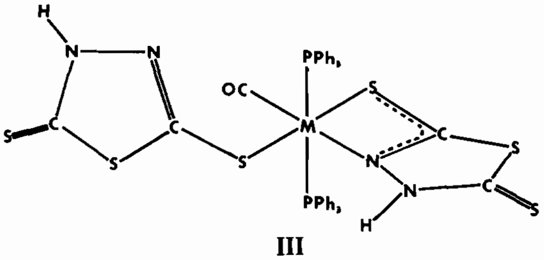
II

Infrared Spectra

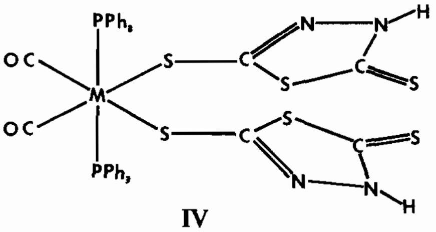
Infrared spectra for the 1,3,4-thiadiazole-2,5-dithiolato complexes are collected in Table III. In addition to bands attributable to triphenylphosphine and, where appropriate, ν(M–H) and ν(CO), the spectra display four absorptions at *ca.* 1480, 1260, 1050 and 750 cm^{-1} characteristic of the coordinated tddtH ligand, two of which (*ca.* 1480 and 750 cm^{-1}) are partly masked by strong PPh_3 absorptions. Although assignments have previously been reported, attempts by earlier workers to deduce structural information concerning the tddtH ligand from infrared data have been frustrated by the multi-functional nature of the tddtH ligand and the complexity of the spectra [11–13]. In our complexes the presence of the PPh$_3$ ligands further complicates the infrared spectra and we have therefore not pursued this aspect of our investigation any further.

NMR (^{1}H and ^{31}P{^{1}H}) Spectra; Solution Structure

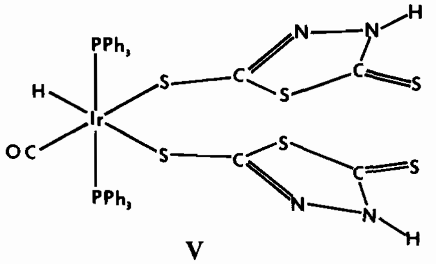
The presence of the ancillary triphenylphosphine ligands enhances solubility sufficiently to permit the collection of ^{1}H and ^{31}P{^{1}H} NMR data (Table IV). These, together with infrared data [ν(CO), ν(M–H)] referred to above, confirm stereochemistry **(III)** for the complexes M(tddtH)$_2$(CO)(PPh$_3$)$_2$ (M = Ru, Os) in solution. With the aid of information concerning the bonding modes of the 1,3,4-thiadiazole-2,5-dithiolate ligand gained from the X-ray diffraction study, the same data establish structures **(IV)** and **(V)** for the complexes M(tddtH)$_2$(CO)$_2$(PPh$_3$)$_2$ and IrH(tddtH)$_2$(CO)(PPh$_3$)$_2$ respectively.



III

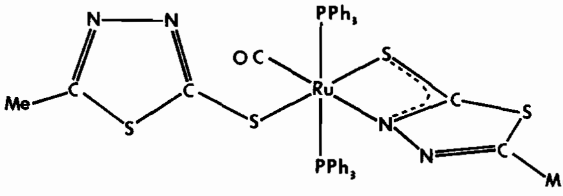


IV



V

Structures in which two potentially bi-dentate-chelate ligands share three adjacent coordination sites frequently display fluxional behaviour involving rapid interchange of mono- and bi-dentate ligands. In an attempt to detect such behaviour variable temperature ^{1}H NMR spectra were recorded for the complexes M(tddtH)$_2$(CO)(PPh$_3$)$_2$ (M = Ru or Os). The 1,3,4-thiadiazole-2,5-dithiolate ligands are not particularly amenable to NMR investigation. However, they do possess a single proton bound to nitrogen [ν(N–H) 2860 and 2925 cm^{-1}] which displays a clear low field resonance at δ *ca.* 12 ppm. Proton NMR spectra of the complex Ru(tddtH)$_2$(CO)(PPh$_3$)$_2$ in CDCl$_3$ solution at ambient temperature display a single resonance, attributable to the NH protons, at δ 11.9 ppm. On cooling the sample to *ca.* 223 K this resonance broadens and finally splits into two resonances at δ 13.1 (broad) and δ 11.9 (sharp) attributable to the protons of mono- and bi-dentate ligands respectively. The broadness of the signal arising from the mono-dentate ligand presumably reflects restricted rotation associated with this mode of bonding. Similar results were obtained for Os(tddtH)$_2$(CO)(PPh$_3$)$_2$ (see Table IV). To confirm that the temperature dependence of these spectra does indicate a true mono-dentate $\rightleftharpoons$ bi-dentate interchange and not merely a proton (NH) transfer process, we prepared, and examined by ^{31}P{^{1}H} and variable temperature ^{1}H NMR spectroscopy, an analogous ruthenium complex, Ru(mtdt)$_2$(CO)(PPh$_3$)$_2$, **(VI)** containing the closely related 5-methyl-1,3,4-thiadiazole-2-thiolate (mtdt) ligand. The red crystalline air-stable complex is moderately soluble in organic solvents and is therefore amenable to study by NMR. Furthermore the methyl protons, unlike the NH protons, are not expected to participate in exchange interactions independently of the rest of the ligand. The ^{31}P NMR spectrum was temperature independent and displayed a singlet [δ(P) 38.3 ppm] consistent with a *trans* phosphine stereochemistry analogous to that found for Ru(tddtH)$_2$(CO)(PPh$_3$)$_2$.



VI

However, the ^{1}H NMR spectrum (CDCl$_3$, 328 K) contained a singlet (δ 2.32 ppm) attributable to the six methyl protons which, on cooling the sample, broadened (299 K) then decoalesced (263 K) into two sharp singlets (δ 2.45 and 2.22 ppm). We take this result as clear evidence of a dynamic equilibrium process involving interchange of mono-dentate (S-bonded) and bi-dentate (N,S-bonded) 5-methyl-1,3,4-thiadiazole-2-thiolate ligands in the complex

$Ru(mtdt)_2(CO)(PPh_3)_2$. This in turn provides strong evidence to confirm our original conclusion concerning similar fluxional behaviour in the complex $Ru(tddtH)_2(CO)(PPh_3)_2$ and its osmium analogue. Information about the bonding modes of the 1,3,4-thiadiazole-2,5-dithiolate ligand gained from the present work led us to question the conclusions reached by other authors [12, 13] concerning the identity of the so-called rhodium(I) complex $RhCl(tddtH_2)_2(PPh_3)$ and palladium(0) or platinum(0) complexes $M(tddtH_2)_2(PPh_3)_2$. Samples of these products, prepared using the original procedures, were examined by $^{31}P\{^1H\}$ NMR. Unfortunately the rhodium and palladium complexes proved to be too insoluble to give meaningful spectra. However, the platinum complex yielded a clear spectrum which displayed two singlets (δ 28.7 and 23.0 ppm) with platinum-195 satellites. The magnitudes of the associated coupling constants [$^1J(PtP)$ 2946 and 2653 Hz respectively] are indicative of square-planar platinum(II) with *trans* triphenylphosphine ligands. The high field ^1H NMR wpectrum contained a hydride resonance [δ -10.95 (6) $^2J(P–H)$ = *ca.* 12 Hz with platinum-195 satellites, $^1J(Pt–H)$ = 1069Hz] consistent with the presence of *trans*-$PtH(tddtH)(PPh_3)_2$. We therefore conclude that platinum complex is in reality the platinum(II) species *trans*-$Pt(tddtH)_2(PPh_3)_2$ formed by the oxidative addition sequence: $Pt(PPh_3)_4 \rightarrow PtH(tddtH)(PPh_3)_2 \rightarrow Pt(tddtH)_2(PPh_3)_2$ and, in our hands at least, is contaminated by significant quantities of the intermediate hydride. It seems probable that the rhodium and palladium products should similarly be reformulated as octahedral rhodium(III) $RhCl(tddtH)_2(PPh_3)$ and square-planar palladium(II) $Pd(tddtH)_2(PPh_3)_2$ respectively. A weak infrared absorption at *ca.* 2470 cm^{-1} in the spectra of these complexes has been attributed to ν(S–H) and taken as evidence for the presence of N-coordinated 1,3,4-thiadiazole-2,5-dithiol [12, 13]. However we have noted similar weak absorptions in the spectra of several triphenylphosphine complexes which do not contain thiol groups and attribute them instead to combination bands.

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