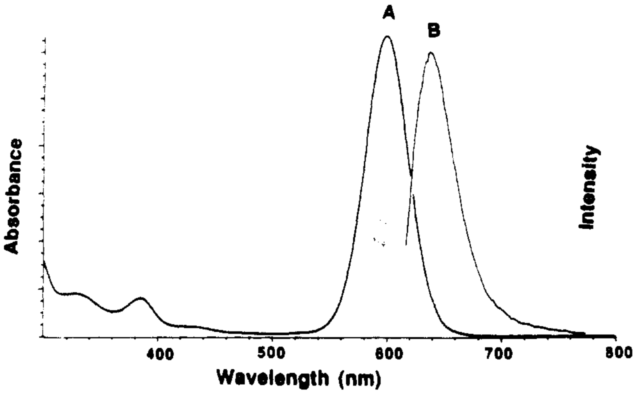


Figure 3. (A) Electronic absorption and (B) uncorrected emission (λ_{exc} 600 nm) spectra of a dichloromethane solution of $[\mathrm{Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-}dppb)_2}]$.

the adduct. This change may have been accomplished by rotation of the ClIr(CO) unit about its P–Ir–P axis. The 6.683 (1)-Å separation between the two iridium atoms in the open metallamacrocycle appears sufficient to allow for passage of one Ir–Cl unit through the central space. The second change involves a pronounced bending of the P–Ir–P angle. In the adduct this angle is 151.4 (3)°, while it is nearly linear (175.9 (1)°) in the free metallamacrocycle. This bending allows the two iridium atoms to approach the tin atom and results in a net contraction of the Ir···Ir separation by 1.532 Å (to 5.151 (1) Å) in the adduct. This bending appears to have only minor consequences on the Cl–Ir–CO unit, which remains essentially linear.

The adduct retains its structure in dichloromethane or tetrahydrofuran solution. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum consists of a singlet at 9.75 ppm with satellites due to coupling to tin (^2J(Sn,P) = 96.7 Hz). The electronic absorption spectrum of the adduct is shown in Figure 3. An intense feature at 600 nm (ϵ = 45 000 $\mathrm{M^{-1}\ cm^{-1}}$) is responsible for the blue color. The complex is luminescent with an intense emission, with λ_{max} = 647 nm. The small Stokes shift and the mirror image relation to the absorption spectrum suggest that the emission arises from fluorescence. Solutions of this adduct are very sensitive to air. Exposure to the atmosphere results in bleaching of the blue color. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum indicates that the free metallamacrocycle, $\mathrm{Ir_2(CO)_2Cl_2(\mu\text{-}dppb)_2}$, which does not bind dioxygen, is liberated in this process.

$\mathrm{Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-}dppb)_2}$ and $[\mathrm{Ir_2(SnCl)(CO)_2Cl_2(\mu\text{-}dpma)_2}]^+$ have a number of important differences. The first is a neutral molecule, while the latter is a monocation. The tin is four-coordinate in the former, but three-coordinate and planar in the latter. Nevertheless, the electronic absorption and emission spectra of the two are similar. Thus the added chloride ligand in $\mathrm{Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-}dppb)_2}$ serves only to fill a vacant tin orbital and does not perturb the essential chromophore, which involves the filled d_{z^2} orbitals on iridium, the filled s orbital on tin, and the empty p orbitals on both iridium and tin.[3] $\mathrm{Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-}dppb)_2}$ is sensitive to oxidation by air, whereas $[\mathrm{Ir_2(SnCl)(CO)_2Cl_2(\mu\text{-}dpma)_2}]^+$ is not. Treatment of the latter with an excess of 18-crown-6 in dichloromethane results in the removal of the $\mathrm{SnCl^+}$ unit, while 18-crown-6 has no effect on solutions of $\mathrm{Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-}dppb)_2}$.

$\mathrm{Ir_2(CO)_2Cl_2(\mu\text{-}dppb)_2}$ does not react with either ($\mathrm{Me_2SAuCl}$) or $[\mathrm{AuCl_4}]^-$, species which readily add to **1**.[10] It does, however, form pink and orange complexes on treatment with lead(II) acetate or thallium(I) nitrate. Thus, it appears to have the selectivity that we anticipated. Further studies on complexes of the type **3** with varying ring sizes are in progress.

Acknowledgment. We thank the National Science Foundation (Grant CHE 894209) for support, Johnson Matthey, Inc., for a loan of iridium salts, and Ella Fung for assistance.

---

(10) Balch, A. L.; Nagle, J. K.; Oram, D. E.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 454.

Supplementary Material Available: Tables of all atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and crystal refinement data for $\mathrm{Ir_2(CO)_2Cl_2(\mu\text{-}dppb)_2}$ and its tin(II) chloride adduct (13 pages); listings of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

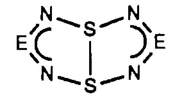
Department of Chemistry
University of California
Davis, California 95616

Alan L. Balch*
Brian J. Davis
Marilyn M. Olmstead

Received April 27, 1990

A Novel Coordination Mode for Dithiatetrazocines: Preparation, X-ray Structure, and Fluxional Behavior of $[\mathrm{Pt(PPh_3)(1,5\text{-}Ph_4P_2N_4S_2)}]_2$

The coordination chemistry of inorganic sulfur–nitrogen (S–N) ligands has been an area of considerable recent activity.[1,2] The interaction of tetrathiatetrazocine, $\mathrm{S_4N_4}$, with the platinum group metals usually results in fragmentation of the ligand to give metal complexes of S–N anions.[1,2] There are two complexes, $\mathrm{Ir(CO)Cl(S_4N_4)(PPh_3)}$[3] and $\mathrm{Pt(S_4N_4)Cl_2(PMe_2Ph)}$,[4] which incorporate the tridentate (N,S,S) $\mathrm{S_4N_4}^{2-}$ ligand formed by insertion of the metal into an S–N bond. In contrast, we have shown that the integrity of dithiatetrazocines $\mathrm{E_2N_4S_2}$ (**1a**, E = $\mathrm{Me_2NC}$; **1b**, E = $\mathrm{Ph_2P}$) is retained in the formation of 1:1 complexes with platinum, $\mathrm{Pt(E_2N_4S_2)(PPh_3)_2}$ (**2a**, E = $\mathrm{Me_2NC}$; **2b**, E = $\mathrm{Ph_2P}$), in which the metal–ligand bonding is analogous to that found in η^2-alkene–platinum complexes.[5] We report here the preparation and X-ray structural characterization of the binuclear complex $[\mathrm{Pt(1,5\text{-}Ph_4P_2N_4S_2)(PPh_3)}]_2$ (**3**) in which the ligand **1b** exhibits a novel bonding mode. A variable-temperature ^{31}P NMR spectroscopic study of **3** provides evidence for the first example of a metallotropic rearrangement in coordination complexes of S–N ligands.



1a, E = $\mathrm{Me_2NC}$
b, E = $\mathrm{PPh_2}$

The thermal decomposition of **2b** in solution results in the dissociation of triphenylphosphine and the formation of the binuclear complex, **3**.[6] This process is reversible; the addition of 2 molar equivalents of $\mathrm{Ph_3P}$ to a solution of **3** in $\mathrm{CH_2Cl_2}$ slowly regenerates **2b**.

$$2\mathrm{Pt(1,5\text{-}Ph_4P_2N_4S_2)(PPh_3)_2} \underset{+2\mathrm{PPh_3}}{\overset{-2\mathrm{PPh_3}}{\rightleftharpoons}} [\mathrm{Pt(1,5\text{-}Ph_4P_2N_4S_2)(PPh_3)}]_2 \tag{1}$$

The structure of **3** was determined by X-ray crystallography.[7] The molecular geometry and atomic numbering scheme are shown in Figure 1. The $\mathrm{P_2N_4S_2}$ rings in **3** act as chelating (N,S) ligands toward one platinum and form a bridge to the second platinum via the other sulfur atom to give a centrosymmetric dimeric structure. The geometry around platinum is approximately square planar. The sulfur atoms are both three-coordinate and trans to each other, and the Pt–S bond lengths are equal. The coordination to platinum results in significant distortions of the geometry of

---

(1) Chivers, T.; Edelmann, F. *Polyhedron* **1986**, *5*, 1661.
(2) Kelly, P. F.; Woollins, J. D. *Polyhedron* **1986**, *5*, 607.
(3) Edelmann, F.; Roesky, H. W.; Spang, C.; Noltemeyer, M.; Sheldrick, G. M. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 931.
(4) (a) Hursthouse, M. B.; Motevalli, M.; Kelly, P. F.; Woollins, J. D. *Polyhedron* **1989**, *8*, 997. (b) Kelly, P. F.; Woollins, J. D. *Polyhedron* **1989**, *8*, 2907.
(5) Chivers, T.; Dhathathreyan, K. S.; Ziegler, T. *J. Chem. Soc., Chem. Commun.* **1989**, 86. Preliminary X-ray structural data have established η^2-S,S′ bonding for **2a**, but the structure of **2b** has not been ascertained.
(6) A solution of **2b**[5] (0.25 mmol) in toluene (30 mL) was heated at 105 °C for 6 h under an atmosphere of dry $\mathrm{N_2}$. The bright yellow precipitate of **3** (0.10 mmol, 80%) was isolated by use of a filter needle and identified by X-ray crystallography. ^{31}P NMR data for **3** are given in the text.

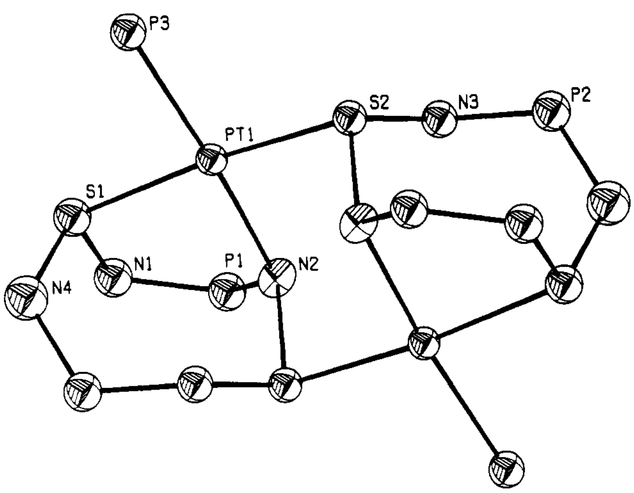
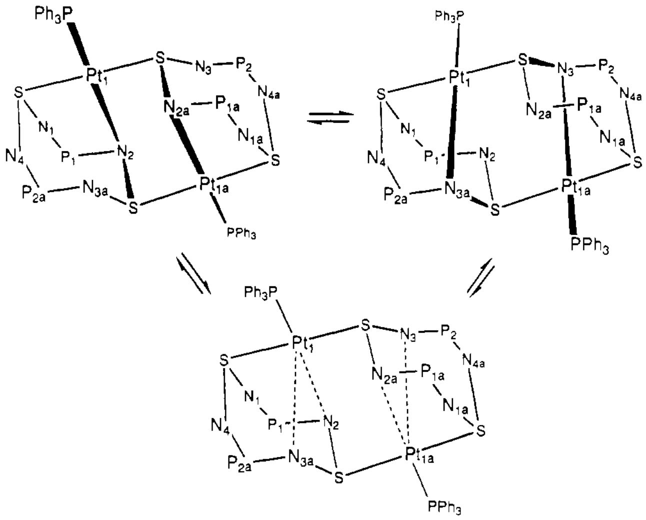


Figure 1. ORTEP plot of $[Pt(1,5\text{-}Ph_4P_2N_4S_2)(PPh_3)]_2$ (**3**) (50% probability ellipsoids). Phenyl groups attached to phosphorus are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pt(1)–S(1) = 2.344 (3), Pt(1)–S(2) = 2.342 (3), Pt(1)–P(3) = 2.250 (3), Pt(1)–N(2) = 2.089 (7), S(1)–N(1) = 1.650 (8), S(1)–N(4) = 1.65 (1), S(2)–N(3) = 1.599 (8), S(2)–N(2A) = 1.753 (8), P(1)–N(1) = 1.591 (8), P(1)–N(2) = 1.637 (9), P(2)–N(3) = 1.607 (8), P(2)–N(4A) = 1.61 (1); S(1)–Pt(1)–P(3) = 91.1, S(1)–Pt(1)–N(2) = 83.4 (2), S(2)–Pt(1)–P(3) = 91.2 (1), S(2)–Pt(1)–N(2) = 94.4 (2), S(1)–Pt(1)–S(2) = 172.9 (1), P(3)–Pt(1)–N(2) = 174.4 (2), N(1)–S(1)–N(4) = 107.9 (4), N(3)–S(2)–N(2A) = 107.2 (4), N(1)–P(1)–N(2) = 112.1 (4), N(3)–P(2)–N(4A) = 121.2 (5), S(1)–N(1)–P(1) = 115.2 (5), P(1)–N(2)–S(2A) = 115.8 (5), S(2)–N(3)–P(2) = 125.5 (6), S(1)–N(4)–P(2A) = 125.5 (6), Pt(1)–S(1)–N(1) = 104.4 (3), Pt(1)–S(1)–N(4) = 104.7 (3), Pt(1)–S(2)–N(3) = 107.7 (3), Pt(1)–S(2)–N(2A) = 98.5 (3), Pt(1)–N(2)–P(1) = 108.5 (4), Pt(1)–N(2)–S(2A) = 114.4 (4).

the ligand **1b**.[8] The transannular S–S separation is opened up from 2.528 (1) in **1b**[8] to >3.7 Å in **3**. The average S–N bond length increases from 1.588 (6) to 1.63 (2) Å [S(1)–N(1), S(1)–N(4)] or 1.753 (8) Å [S(2A)–N(2)]. The latter distance is unusually long even for a bond involving three-coordinate nitrogen [cf. *d*(S–N) = 1.682 (6) Å for the corresponding bond in $1,5\text{-}Ph_4P_2N_4S_2Me^+CF_3SO_3^-$].[9] The NSN angles are reduced from 116.1 (1)° in **1b** to an average value of 107.5 (4)° in **3**. There are substantial differences in the bond angles at phosphorus and nitrogen between the five-membered PtN_2PS and the seven-membered PtN_3PS_2 rings in **3**. In the former ring, the bond angle at phosphorus is 112.1 (4)° and the SNP angle is 115.2 (5)°. The corresponding values for the PtN_3PS_2 ring are 121.2 (5) and 125.5 (4)°, respectively. The central six-membered $Pt_2N_2S_2$ ring adopts a chair conformation with the platinum atoms in the 1,4-positions.

The $\{^1H\}$ ^{31}P NMR spectrum of **3** (200 MHz, 1:1 $CH_2Cl_2/CDCl_3$) at –60 °C is consistent with the observed crystal structure. Two broad and equally intense singlets, attributable to the inequivalent Ph_2P groups of the heterocyclic ligand, are observed at +46.3 and +16.1 ppm (reference external 85% H_3PO_4).[10] A singlet at +8.6 ppm with $^1J_{Pt-P}$ = 4160 Hz is seen for Ph_3P [cf. **2b**, $\delta(^{31}P)$ = +15.3 (Ph_3P) ($^1J_{Pt-P}$ = 2850 Hz) and +39.0 (Ph_2P) (J_{Pt-P} = 580 Hz)].[11] When the temperature of the solution is gradually raised, the two Ph_2P singlets broaden and collapse until

Scheme I. Proposed Mechanism for the [1,3]-Metallotropic Rearrangement in $[Pt(1,5\text{-}Ph_4P_2N_4S_2)(PPh_3)]_2$ (**3**)



at +35 °C a singlet is observed at +31.1 ppm (J_{Pt-P} = 170 Hz). The signal for Ph_3P shifts slightly to +9.0 ppm over this temperature range. The reverse of these changes is observed when the solution is cooled again to –60 °C. The coalescence temperature is ca. –30 °C, which corresponds to an interconversion barrier of 10.2 ± 0.2 kcal mol^{-1}.[12] We propose that this fluxional process occurs via a [1,3]-metallotropic rearrangement involving a pendular movement of Pt(1) from N(2) to N(3A) and, concomitantly, Pt(1A) from N(3) to N(2A), which results in the chair → chair isomerization of the central $Pt_2N_2S_2$ ring (see Scheme I).

In summary, this study has (a) established a new coordination mode for dithiatetrazocines in which the ligand **1b** serves a dual function as both a chelating and a bridging ligand *without cleavage of the eight-membered ring*, (b) revealed the first example of a metallotropic rearrangement in coordination complexes of S–N ligands, and (c) demonstrated that the availability of a ^{31}P NMR probe greatly facilitates the study of the coordination chemistry of **1b** relative to that of S_4N_4. These findings portend a coordination chemistry for dithiatetrazocines that is significantly different from that of binary S–N ligands.

Acknowledgment. Financial support from the NSERC (Canada) in the form of an operating grant and an International Scientific Exchange Award is gratefully acknowledged.

Supplementary Material Available: Listings of atomic coordinates, isotropic thermal parameters, anisotropic thermal parameters, all bond distances and bond angles, and torsion angles for non-hydrogen atoms (8 pages); a listing of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

Department of Chemistry
The University of Calgary
Calgary, Alberta T2N 1N4, Canada

Tristram Chivers*
Mark Edwards
Pramesh N. Kapoor[13]

Laboratory of Polymer Chemistry
University of Groningen
Nijenborgh 16
9747 AG Groningen,
The Netherlands

Auke Meetsma
Johan C. van de Grampel
Arie van der Lee

Received June 14, 1990

---

(7) Yellow crystals of **3** were obtained by diffusion of hexane into a C_6H_6–CH_2Cl_2 solution. Crystal data: $(C_{42}H_{35}N_4P_3PtS_2)_2(C_6H_6)_2$ (**3**), M_r = 2052.0, monoclinic, space group $P2_1/c$; at 298 K, a = 12.918 (3) Å, b = 14.316 (1) Å, c = 23.484 (2) Å, β = 99.62 (1)°, V = 4282 (1) Å^3, Z = 2, μ(Mo K$\bar{\alpha}$) = 35.5 cm^{-1}, $F(000)$ = 2048, D_c = 1.591 g cm^{-3}. Intensity data were collected at 298 K on an Enraf-Nonius CAD-4F diffractometer operating in the ω–2θ mode and using Mo K$\bar{\alpha}$ radiation (λ = 0.71073 Å, graphite monochromator). The total number of unique reflections was 10297, of which 5434 have $F \geq 4.0\ \sigma(F)$. Crystal dimensions were 0.10 × 0.20 × 0.33 mm. The structure was solved by standard Patterson methods and subsequent partial structure expansion (SHELX86) and difference Fourier techniques. The least-squares refinement on F with anisotropic thermal parameters for all non-hydrogen atoms (XTAL) converged at R = 0.059 and R_w = 0.044.

(8) Burford, N.; Chivers, T.; Richardson, J. F. *Inorg. Chem.* **1983**, *22*, 1482.

(9) Chivers, T.; Dênès, G. Y.; Liblong, S. W.; Richardson, J. F. *Inorg. Chem.* **1989**, *28*, 3683.

(10) The ^{195}Pt satellites could not be resolved for these broad signals.

(11) The value of 580 Hz for J_{Pt-P} in **2b** represents either a two-bond coupling for a μ-N,N′ binuclear compound or a three-bond coupling for an η^2-S,S′ mononuclear complex as depicted by structures **4** and **5**, respectively, in ref 5.

(12) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

(13) Permanent address: Department of Chemistry, University of Delhi, Delhi-110007, India.