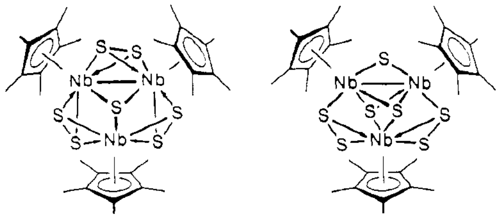
spectrum.[14] On the other hand, it seems unlikely that Nb–H bonds formed during the reaction can be resistive toward the attack of still more excess sulfur.[15]

Only weak hints for the nature of the major product **3**[13] could be obtained thus far. The fact that no hydride resonance was detected in the ^{1}H NMR spectrum suggests together with analytical data a binuclear complex of formula $Cp^*_4Nb_2S_5$. The diamagnetism of **3** along with IR spectroscopic data requires the presence of $Nb(\eta^2\text{-}S_2)$ moieties as in **1** and a S^{2-} bridge. It is still unclear if there is any relation between **2** and **3**. In this regard it must be pointed out that complexes with terminal SH ligands are able to react with sulfur to give polysulfide complexes.[15,16]

A completely different chemistry is observed when $Cp^*Nb(CO)_4$ is irradiated in the presence of $^1/_2$ S_8 (THF, 3 h). The diamagnetic brown-green $Cp^*_3Nb_3S_7$ (**4**)[13] was isolated in about 30% yield after chromatography (SiO_2, toluene). Suitable single crystals could not be obtained because of the pertinacious tendency of the material to give amorphous aggregates in any solvent. The only structural information available arises from the ^{1}H NMR spectrum, which indicates two different Nb centers by a 2:1 ratio for the methyl resonances. These are invariable up to 100 °C. Among several possible isomeric forms structural proposal **C** seems reasonable on the basis of a Nb_3S tetrahedron with laterally coordinated S_2 ligands and only one Nb–Nb bond. All Nb atoms in this mixed valence compound (formal charges +III and +IV) thus attain a closed valence shell. A similar M_3S_7 core geometry has already been established for $[Mo_3S(\mu\text{-}S_2)_3(S_2)_3]^{2-}$.[17] A second proposal (**D**) can be derived from the structure of $Cp_3Ta_3S_7Cl_2$[18] by hypothetical reductive halogen elimination and concomitant formation of a metal–metal bond. Interestingly, $Cp^*V(CO)_4$ gives in comparable reactions with S_8 only dinuclear products, e.g. $Cp^*_2V_2S_5$ and $Cp^*_2V_2S_4$.[19]



C D

4

In conclusion promising entries to a novel niobium polysulfide complex chemistry have been developed. The high content of S–S bonds, e.g. in **1**, may involve a high reactivity potential, as already demonstrated by preliminary studies.[10] It also raises the question of the mechanism of formation of such compounds. Thus, more detailed investigations on the influence of the substituents as the Cp ligand as well as on the nature of the ligands attached to the CpNb fragment will be necessary.

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Supplementary Material Available: Complete tables of crystal data, atomic coordinates, and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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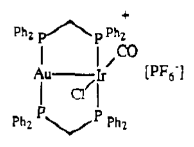
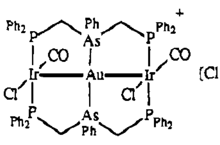
Structure and Photoluminescence of a Heterodinuclear d^{10}–d^8 Complex, $[AuIr(CO)Cl(\mu\text{-}Ph_2PCH_2PPh_2)_2][PF_6]$

Recently, there has been considerable interest in the metal–metal interaction, electronic absorption spectra, and photoluminescence of dinuclear, homometallic complexes with either d^8–d^8[1] or d^{10}–d^{10}[2] electronic configurations. As yet, there do not appear to be any observations of photoluminescence from heterodinuclear species or from complexes containing a d^{10}–d^8 pair. Here we present preliminary information on the structure and spectroscopy of such a species, $[AuIr(CO)Cl(\mu\text{-dpm})_2][PF_6]$ (**1**; dpm = bis(diphenylphosphino)methane). On the basis of our work on the heterotrinuclear complex **2**,[3] we suspected that **1** should also show photoluminescence.



1



2

$[AuIr(CO)Cl(\mu\text{-dpm})_2][PF_6]$ was obtained as orange crystals by the method of Shaw and co-workers.[4] The structure of the cation, as determined by X-ray crystallography,[5] is shown in Figure 1. The complex consists of a planar $Ir(CO)ClP_2$ unit connected to a linear AuP_2 moiety through the two dpm bridges. Interatomic

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[1] (a) Pt_2^{4+}: Roundhill, D. M.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989**, *22*, 55. Zipp, A. P. *Coord. Chem. Rev.* **1988**, *84*, 47. (b) Rh_2^{2+}: Fordyce, W. A.; Crosby, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 985. (c) Ir_2^{2+}: Marshall, J. L.; Stobart, S. R.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 3027.

[2] (a) Pt_2^0 and Pd_2^0: Casper, J. V. *J. Am. Chem. Soc.* **1988**, *110*, 2145. (b) Au_2^{2+}: Khan, M. N. I.; Fackler, J. P., Jr.; King, C.; Wang, J. C.; Wang, S. *Inorg. Chem.* **1988**, *27*, 1672. Che, C. M.; Wong, W. T.; Lai, T.-F.; Kwong, H.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 243.

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[5] Orange needles of $[AuIr(CO)Cl(\mu\text{-dpm})_2][PF_6]\cdot 0.5CH_2Cl_2$ were obtained by diffusion of diethyl ether through a 5 mm thick layer of methanol into a saturated dichloromethane solution of **1** in a 4 mm o.d. tube. They belong to the orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 10.541$ (3) Å, $b = 18.621$ (7) Å, and $c = 27.113$ (9) Å at 130 K with $Z = 4$. Refinement using 4577 reflections with $I > 2\sigma(I)$ and 227 parameters yielded $R = 0.063$ and $R_w = 0.066$.

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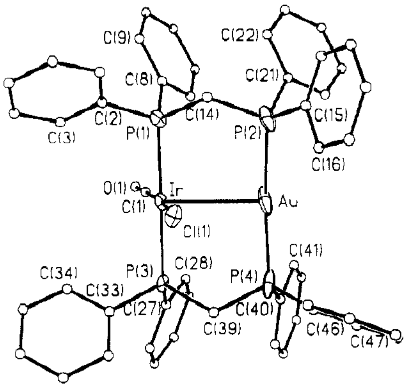

Figure 1. Structure of the cation of $[AuIr(CO)Cl(\mu\text{-dpm})_2][PF_6]$ with 50% thermal contours for the heavy atoms and uniform arbitrarily sized circles for carbon and oxygen. Selected bond distances (Å): Au-Ir, 2.986 (1); Au-P(2), 2.309 (5); Au-P(4), 2.324 (6); Ir-P(1), 2.320 (5); Ir-P(3), 2.311 (5); Ir-Cl, 2.373 (5); Ir-C(1), 1.84 (2). Selected angles (deg): P(2)-Au-P(4), 169.7 (2); P(1)-Ir-P(3), 173.6 (2); P(1)-Ir-Cl, 86.8 (2); P(1)-Ir-C(1), 93.0 (6); P(3)-Ir-Cl, 87.1 (2); P(3)-Ir-C(1), 92.8 (6).

distances and angles within these two coordination units are normal. The binuclear unit has an eclipsed structure with dihedral angles of 2.5 and 0.1° between adjacent P-Au-Ir and Ir-Au-P planes. The size and shape of the thermal ellipsoids indicate that the AuP_2 unit exhibits a greater degree of thermal motion than the $IrP_2(CO)Cl$ unit. Since the $M_2(dpm)_2$ framework is very flexible and capable of spanning M-M distances from 2.1 to 3.6 Å, it is informative to compare the Au-Ir distance in **1** (2.986 (1) Å) to other related species. This distance is slightly shorter than the Au-Ir distances in **2** (3.059 (1), 3.012 (1) Å).[3] It is similar to the Au-Au separations in $Au_2(\mu\text{-dpm})_2Cl_2$ (2.962 Å)[7] and shorter than the less constrained Au-Au distance in $Au_2(\mu\text{-dpm})Cl_2$ (3.351 (2) Å).[8] There is probably considerable similarity between the Au-Ir interactions in **1** and **2** and the numerous examples of short Au-Au contacts seen in Au(I) complexes.[9] The Au-Ir distance is considerably shorter than the Rh-Rh distances in d^8-d^8, face-to-face dimers such as $Rh_2(CO)_2Cl_2(\mu\text{-dpm})_2$ (Rh-Rh = 3.2386 (5) Å)[10] and $Rh_2(CO)_2Cl_2(\mu\text{-}Ph_2AsCH_2AsPh_2)_2$ (3.236 (2) Å as a dichloromethane solvate[11] 3.396 (1) Å unsolvated[12]). Unfortunately, no Ir-Ir distances in related face-to-face dimers are known. It is, however, likely that metal-metal interactions are stronger, and their distances shorter, for elements of the third transition series than for those of the first and second series.

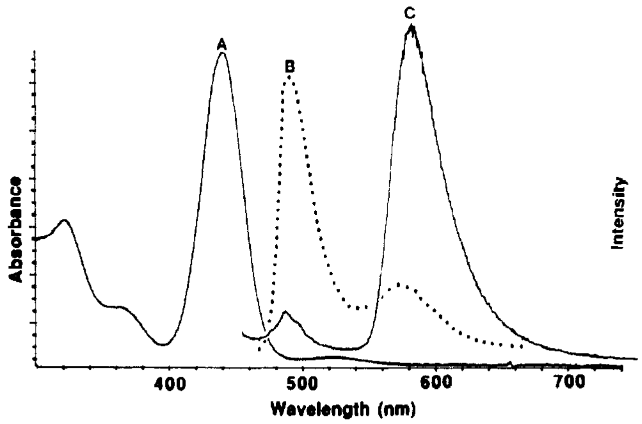

Figure 2. Electronic spectrum of $[AuIr(CO)Cl(\mu\text{-dpm})_2][PF_6]$ in dichloromethane soution: (A) absorption at 25 °C (λ_{max} (ϵ) 518 nm (800 M^{-1} cm^{-1})8, 440 (18600), 362 (3700), 320 (8700)); (B) emission at -78 °C with excitation at 430 nm; (C) emission at -196 °C with excitation at 430 nm.

Figure 2 shows the absorption and emission spectra obtained for solutions of **1** in dichloromethane. The absorption spectrum is dominated by a feature at 440 nm (ϵ = 18600 M^{-1} cm^{-1}), which we attribute to a spin-allowed $d_{\sigma^*(z)} \rightarrow p_z$ transition (where *z* lies along the Ir-Au bond). The weaker band at 518 nm may be the spin-forbidden counterpart of this transition. In comparison, **2** shows an intense absorption at 508 nm (ϵ = 32000 M^{-1} cm^{-1}).[3] The fact that **2** absorbs at lower energies than **1** is entirely consistent with related observations that compare dinuclear (d^8-d^8) and trinuclear (d^8-d^8-d^8) complexes (e.g $[Rh_2(CNCH_3)_4(\mu\text{-dpm})_2]^{2+}$ and $[Rh_3(CNCH_3)_6\{\mu\text{-}(Ph_2PCH_2)_2PPh\}_2]^{3+}$).[13,14] Thus, the d_{σ^*}/p_z gap narrows as metal ions are added to these linear groupings. The absorption of **1** occurs at a considerably different energy, but one between those seen for the face-to-face dimers $Ir_2(CO)Cl_2(\mu\text{-dpm})_2$ (λ_{max} = 518 nm)[15] and $Au_2(\mu\text{-dpm})_2^{2+}$ (λ_{max} = 292 nm),[16] as would be expected for a transition involving predominantly metal orbitals. The emission spectrum obtained with excitation at 430 nm at -78 °C consists of two bands: a strong one at 498 nm and a weak one at 570 nm. Similar but weak emission is seen at room temperature. The lifetime of the low-energy feature is 4 μs at -196 °C in frozen dichloromethane, while the lifetime of the higher energy emission is <50 ns at 25 °C in dichloromethane. The higher energy emission, which overlaps the major absorption feature, is assigned as fluorescence, while the other, lower energy, emission is expected to arise from phosphorescence. When the sample is frozen in liquid nitrogen, these bands move to 484 and 582 nm, and the low-energy band grows in intensity relative to the high-energy feature. The increase in relative intensity of the high-energy emission relative to the low-energy band with increasing temperature is readily explained as temperature-dependent quenching of the phosphorescence, and these changes with temperature further substantiate the assignment of fluorescence and phosphorescence.

The cation, $[AuIr(CO)Cl(\mu\text{-dpm})_2]^+$, is resistant to chemical modification by chloride ion, which is known to bind to gold(I) complexes (e.g. $Au_2(dpm)_2^{2+} + 2Cl^- \rightarrow Au_2(dpm)_2Cl_2$),[7,16] and by carbon monoxide, which adds to Vaska-like complexes (e.g. $Ir(CO)Cl(PPh_3)_2 + CO \rightarrow Ir(CO)_2Cl(PPh_3)_2$),[17] since the absorption spectrum is unaffected by the addition of a 10-fold molar excess of tetraphenylarsonium chloride or by 1 atm of carbon monoxide. These alterations in reactivity reflect the significance of the Ir-Au interaction in **1**.

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Supplementary Material Available: Tables of crystal data and structure determination parameters, atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positions for **1** (9 pages); listings of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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