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Calculated Structure and Optical Properties of $Tl_2Pt(CN)_4$

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The study of closed-shell interactions in heavy-element chemistry is only in its infancy, and therefore, every new situation is of interest. For a review, see ref 1. The most common examples are the interactions between the d^{10} species Cu(I)[2] Au(I)[3,4] and the s^{2} species Tl(I)[5] and between closed-shell pnicogen and chalcogen molecules.[6]

Experimental structural data suggest that 5d^{8} Ir(I) or Pt(II) ions also participate in interactions similar to those for Au(I).[7] We consider here the d^{8}−s^{2}-bonded compound $Tl_2Pt(CN)_4$, which appeared to form an unusual molecular crystal.[8] Its Tl−Pt bond was analyzed by density-functional (DFT) calculations,[9] at the experimental crystal geometry, to be mainly an ionic one, between the Tl^{+} (6s^{2}) and $[Pt(CN)_4]^{2-}$ closed-shell moieties, with some covalent character. It should, however, be added that DFT methods have difficulties in reproducing dispersion interactions.[10]

We now report geometry-optimized scalar-relativistic GAUSSIAN 92[11] calculations at the Hartree−Fock (HF) and second-order Møller−Plesset (MP2) levels. We used either three-valence-electron (3-VE) or 21-VE pseudopotentials on Tl and 18-VE ones on Pt.[12] C and N were treated at the all-electron level. Complete active space self-consistent field (CASSCF) with subsequent multireference configuration interaction (MRCI) and averaged coupled-pair functional (ACPF) calculations for the ground state as well as the lowest singlet and triplet excited states using basis sets of polarized valence triple-ζ quality have been performed with the MOLPRO program system.[13,14] Spin−orbit (SO) effects were estimated from singles and doubles configuration interaction (CISD) calculations in D_{2h}* double group symmetry using the COLUMBUS program system.[15] In these calculations pseudopotentials (C, 4 VE; N, 5 VE; Pt, 18 VE; Tl, 3 VE) and corresponding spin−orbit operators for Pt and Tl have been applied together with basis sets of valence double-ζ quality. The counterpoise correction was applied to estimate the basis-set superposition error (BSSE).[16]

Table 1. Calculated Bond Lengths (pm) and Symmetric (a_{1g}) Tl−Pt Stretching Force Constants (au) for the Isolated $Tl_2Pt(CN)_4$ Molecule in Comparison to Experimental Data for the Solid[a]

method	Tl−Pt	Pt−C	*k*(Tl−Pt)
HF(3-VE)	303.5	203.9	
HF(21-VE)	302.6	203.9[b]	0.0561
MP2(3-VE)	285.2	200.0	
MP2(21-VE)	278.2	200.0[b]	0.1284
MP2(21-VE) + CP[c]	287.0	200.0[b]	0.0979
MRCI(3-VE)	290.0	200.0[b]	0.0767
ACPF(3-VE)	288.8	200.0[b]	0.0792
MP2(3-VE,CPP[d])	276.2	200.0[b]	0.0973
MRCI(3-VE,CPP)	277.6	200.0[b]	0.0915
ACPF(3-VE,CPP)	276.7	200.0[b]	0.0942
spin−orbit cor[e]	+0.7		
counterpoise cor[f]	+8.8		−0.0305
total theor[g]	287.7	200.0	
exptl	314.0	200.5	

[a] The optimizations were done in D_{4h} symmetry with fixed C−N distances (119.3 pm). [b] Kept fixed. [c] Full counterpoise correction (CP) applied to $[Pt(CN)_4]^{2-}$ and two isolated Tl^{+} ions. [d] CPP = core-polarization potential. [e] Estimated from CISD calculations with valence double-ζ basis sets. [f] Estimated from MP2(21-VE) calculations. [g] Combining the MP2(21-VE) R_e of 278.2 pm with SO and BSSE corrections. Note that the three CPP values are very close.

The results are given in Table 1. The Pt−C distances are close to experimental values and are not much affected by the approximation level. The calculated Tl−Pt distance is below the experimental value even at the HF level, both for the Tl 3-VE and 21-VE pseudopotentials. Electron correlation effects were then included at the MP2, MRCI, or ACPF level and found to considerably shorten the Tl−Pt bond length and strengthen the *k*(Tl−Pt) force constant, quite analogous with the earlier studies for other heavy elements. The difference between the MP2 3-VE and 21-VE results may mainly be attributed to core-valence correlation effects on Tl, which account for 25% of the bond length contraction from the HF values and were

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(1) Pyykkö, P. Strong Closed-Shell Interactions in Inorganic Chemistry. *Chem. Rev.*, in press.

(2) Kölmel, C.; Ahlrichs, R. *J. Phys. Chem.* **1990**, *94*, 5536.

(3) Pyykkö, P.; Zhao, Y.-F. *Angew. Chem.* **1991**, *103*, 622; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 604.

(4) Pyykkö, P.; Li, J.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133.

(5) Schwerdtfeger, P. *Inorg. Chem.* **1991**, *30*, 1660.

(6) Klinkhammer, K. W.; Pyykkö, P. *Inorg. Chem.* **1995**, *34*, 4134.

(7) Balch, A. L. *Pure Appl. Chem.* **1988**, *60*, 555.

(8) Nagle, J. K.; Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1988**, *110*, 319.

(9) Ziegler, T.; Nagle, J. K.; Snijders, J. G.; Baerends, E. J. *J. Am. Chem. Soc.* **1989**, *111*, 5631.

(10) Kristyán, S.; Pulay, P. *Chem. Phys. Lett.* **1994**, *229*, 175. Pérez-Jordá, J. M.; Becke, A. D. *Chem. Phys. Lett.* **1995**, *233*, 134.

(11) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92, Revision E.2; Gaussian, Inc., Pittsburgh, PA, 1992.

(12) C, N all-electron (10s5p1d)/[3s2p1d] basis from: Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Plenum: New York, 1977; Vol. 3. The C, N polarization functions are from: Huzinaga, S. In *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984. C, N 4,5-VE: Igel-Mann, G.; Stoll, H.; Preuss, H. *Mol. Phys.* **1988**, *65*, 1321 ((4s4p)/[2s2p] basis). $\alpha_s = 0.05$, $\alpha_p = 0.05$, $\alpha_d = 0.8$ (C), 1.0 (N) added for CASSCF/MRCI and ACPF. Pt: Andrae, D.; Häusserman, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123. In the (8s7p6d1f)/[6s6p5d1f] basis, the two outermost p and d functions were decontracted and $\alpha_f = 0.14$ was added; additional $\alpha_f = 0.7$ added for CASSCF/MRCI and ACPF. Tl 3-VE: Schwerdtfeger, P. *Phys. Scr.* **1987**, *36*, 453 ((7s7p2d) basis). Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245 ((4s4p)/[2s2p] basis). $\alpha_d = 0.15$ added for CASSCF/MRCI and ACPF. 21-VE: Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 662 ((8s8p5d)/[4s4p3d] basis). The computations were done on the Convex C3840, Cray X-MP, and IBM SP2 machines at Center for Scientific Computing, Espoo, Finland, and on a DEC Alpha 800 at MPI-PKS, Dresden, Germany.

(13) Program system MOLPRO: Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985**, *115*, 5053. Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803. Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1988**, *145*, 514. Werner, H.-J.; Knowles, P. J. *Theor. Chim. Acta* **1990**, *78*, 175.

(14) The 15 highest occupied orbitals as well as the lowest unoccupied orbital of the ground state were kept active in the CASSCF, resulting in 31 and 20 reference configurations for the ground and excited states, respectively. The total number of contracted (uncontracted) configurations included in the MRCI/ACPF is on the order of 0.5×10^6 (($14-24) \times 10^6$) in D_{2h} symmetry. A size-extensitivity correction was applied to all MRCI results: Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

(15) Chang, A.; Pitzer, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 2500.

(16) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

S0020-1669(95)01049-4 CCC: $12.00

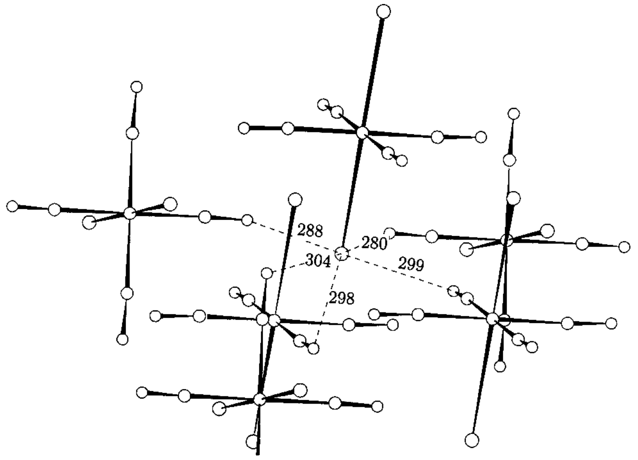

Figure 1. Crystal structure generated from the supplementary material of ref 8.

explicitly included in the latter calculations. The use of a Tl core-polarization potential (CPP) together with the 3-VE pseudopotential is found to reproduce this effect quite well. The SO correction on the Tl−Pt distance is calculated to be small, lengthening it by only 0.7 pm. The BSSE correction, estimated by a full counterpoise correction at the MP2 level for the 21-VE Tl, lengthens the Pt−Tl bond by 8.8 pm. The CP corrected Pt−Tl value is 287.7 pm, which is still far from the experimentally observed distance of 314.0 pm. Thus, neither SO nor BSSE corrections are able to explain the difference.

We next carried out a sensitivity study for the possible effects of the crystal field at the SCF and MRCI level, using 3-VE Tl. The Supplementary Material for ref 8 was used to generate the structure in Figure 1. As can be seen, the next-nearest neighbors of each thallium atom are five cyanides, in approximately D_{4v} symmetry. Rather than trying to calculate a full Madelung sum, we simulated it by five point charges, q, surrounding both Tl centers. The four "equatorial" charges and the Tl form a D_{4h} pattern. The equatorial and axial Tl−q distances are made equal to 300 pm. With increasing values of $|q|$, the experimental Tl−Pt value of 314 pm is already reached at $q = -0.08$ e (SCF) and $q = -0.22$ e (MRCI) at each site. This shows that the crystal-field effects indeed can be sufficient to compensate for the Tl−Pt bond length contraction by intramolecular correlation effects and thus to explain the experimentally observed distance. These results suggest a sizable electrostatic lengthening of the Tl−Pt distance in the crystal, notwithstanding the conclusion of Nagle et al.,[8] based on the sum of atomic radii, that there are no significant interactions between adjacent $Tl_2Pt(CN)_4$ units.

The present Tl−Pt distances can be compared with some other experimental ones between Tl(I) and late-5d-metal atoms. In certain macrocycles, the Ir(I)−Tl(I)−Ir(I) distances are 296−298 pm.[17] In solid $TlAu(CN)_2$, the ···Au(I)−Tl(I)−Au(I)··· chains have distances of 347−349 pm, the Au−Au distance being only 302 pm.[18] If the thallium is oxidized to Tl(II), an experimental Tl−Pt distance of 270.3 pm is obtained.[19]

Table 2. Excitation Energies for the $a_{1g} \rightarrow a_{2u}$ Transitions (cm^{-1}) of the Embedded $Tl_2Pt(CN)_4$ Cluster[a]

	$q = -0.08$		$q = -0.22$		
transition[b]	MRCI	ACPF	MRCI	ACPF	exptl
$^1A_{1g} \rightarrow {}^1A_{2u}$	31 555	30 449	32 422	31 210	
$^1A_{1g} \rightarrow {}^3A_{2u}$	23 651	22 704	24 819	23 789	
$A_{1g} \rightarrow A_{2u}$	28 981	27 875	29 848	28 636	27 000
$A_{1g} \rightarrow A_{1u}$	22 444	21 497	23 612	22 582	22 500
$A_{1g} \rightarrow E_u$	22 554	21 607	23 722	22 692	22 500

[a] All calculations were done for the experimental geometry. The point charges $q = -0.08$ and $q = -0.22$ were optimized at the SCF and ACPF levels, respectively, to give the experimental Pt−Tl distance. [b] Without (rows 1 and 2) and with (rows 3−5) inclusion of spin−orbit interaction. The state labels refer to the D_{4h} group and D_{4h}* double group, respectively.

Concerning atomic charges, the "natural population analysis" (NPA) was more stable as a function of basis and approximation, than the "Mulliken" (MPA) one. Both, however, gave Tl charges close to +1: at the MP2(3-VE) level +0.92 and +0.86 for NPA and MPA, respectively. At the MP2(21-VE) level the NPA charges are $Pt^{0.06+}$, $Tl^{0.92+}$, $C^{0.08-}$, and $N^{0.39-}$.

The crystals are colorless but show a strong near-UV absorption at 27 000 cm^{-1} and an intense blue luminescence at 22 500 cm^{-1}.[8] The singlet-singlet ACPF excitation energies calculated at the experimental crystal geometry, including the point charges modeling the crystal field, for the (spin- and symmetry-allowed) $a_{1g} \rightarrow a_{2u}$ HOMO−LUMO transition are in the range of 27 900−28 600 cm^{-1}, if spin−orbit effects are included (see Table 2). The corresponding (spin-forbidden) singlet−triplet ACPF transitions amount to 21 500−22 700 cm^{-1}. All other excitations were calculated to lie at more than 38 000 cm^{-1} at the ACPF level.

We conclude that the correlation-induced, *metallophilic*[4] attraction is very important in the present Pt(II)−Tl(I), d^8−s^2 case, as well. It is, however, overcompensated by crystal-field effects. A gas-phase experiment should give a Pt−Tl bond length close to the calculated free-molecule value of 287.7 pm, instead of the solid-state value of 314.0 pm.

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(17) Balch, A. L.; Nagle, J. K.; Olmstead, M. N.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 4123.
(18) Assefa, Z.; DeStefano, F.; Garepapaghi, M. A.; LaCasce, J. H., Jr.; Ouellete, S.; Corson, M. R.; Nagle, J. K.; Patterson, H. H. *Inorg. Chem.* **1991**, *30*, 2868.
(19) Usón, R.; Forniés, J.; Tomás, M.; Garde, R.; Alonso, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 1837.