Novel Luminescent Binuclear Gold(I) Isocyanide Complexes. Synthesis, Spectroscopy, and X-Ray Crystal Structure of Au₂(dmb)(CN)₂ (dmb = 1,8-di-isocyano-p-menthane)

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Reaction of K[AuCl₄] with dmb (1,8-di-isocyano-p-menthane) in boiling ethanol yielded Au₂(dmb)(CN)₂ with an intramolecular Au–Au separation of 3.536 Å; excitation of Au₂(dmb)(CN)₂ in fluid solution and in the solid state leads to photoluminescence ($\lambda_{max.}$ ~468 nm, τ_0 0.13 μs in degassed CH_2Cl_2).

Binuclear metal complexes which are co-ordinatively unsaturated and possess long-lived excited states in fluid solutions are found to exhibit novel photochemistry.[1,2] An example is the intensely luminescent tetrakis(pyrophosphito)diplatinate(II) which catalyses the photochemical cleavage of C–H bonds under mild conditions.[2] In our search for photocatalysts for C–H bond activation, we are interested in the 14e two-co-ordinated gold(I) system. Our interest is also stimulated by previous spectroscopic work, indicating that metal-to-ligand charge-transfer excited states of d¹⁰ metal complexes with π-acceptor ligands are usually long-lived.[3,4] We describe here the synthesis and spectroscopic properties of Au₂(dmb)(CN)₂ (dmb = 1,8-di-isocyano-p-menthane) obtained by dealkylation of the isocyanide. Apart from its interesting photophysical properties, this Au^I complex, which has been characterised by X-ray crystallography, also provides a good model system for weak solid-state d¹⁰–d¹⁰ interactions.

Reaction of K[AuCl₄] with excess of dmb in boiling ethanol for 30 min led to the formation of the air-stable solid Au₂(dmb)(CN)₂ in >30% yield. Its i.r. spectrum shows ν(CN) and ν(RNC) stretches at ~2200 and 2290 cm⁻¹ respectively, and its X-ray crystal structure is shown in Figure 1.† The dmb ligand bridges two Au atoms in the *syn* configuration and *trans* to CN⁻.

An important structural feature is the intramolecular Au–Au distance of 3.536 Å, which is much longer than values found in other binuclear Au^I complexes;[5–7] for example, the Au–Au distances in [n-Bu₄N]₂[Au{S₂C₂(CN)₂}]₂ and Au₂[(CH₂)₂PMe₂]₂ are 2.796(1)[5] and 3.005(3) Å[6] respectively. It is, however, close to the intermolecular Au–Au distances in K[Au(CN)₂] (3.64 Å)[3c,8] and Au(MeNC)(CN) [3.52—3.72(4) Å],[9] but is significantly shorter than the normal bite distance of dmb (4.4—4.5 Å), as found in [Rh₂(dmb)₄]²⁺ [10] and Pd₂(dmb)₂I₄.[11] This indicates the presence of a metal–metal bonding interaction in the solid state, an

interaction which may be responsible for the luminescent behaviour of solid K[Au(CN)₂].[3c] As a result of this interaction, the two isocyano groups are bent towards each other, resulting in a significant deviation of the NC–Au–C(isocyanide) angles (173.4 and 173.5°) from 180°. The respective Au–CN and Au–C(isocyanide) distances of 1.95—2.00(1) and 1.96—1.98(1) Å are similar to values found in Au(MeNC)(CN).[9] The C≡N distances of 1.10—1.13(2) Å are normal.

The spectroscopic and photophysical data of Au₂(dmb)(CN)₂ are in Table 1. Its u.v.–visible spectrum (Figure 2) is characterized by two intense vibronic structured absorption bands, I and II, in the region 200—260 nm and very weak absorptions at 260—350 nm in the tail of band II. With reference to previous spectroscopic work on Au^I complexes,[3,4] bands I and II are assigned to the spin-allowed metal-to-ligand charge-transfer transition. The similar optical spectra of Au₂(dmb)(CN)₂ and Au(MeNC)(CN) are in accord with the long Au–Au distance found in the former system.

Table 1. Photophysical properties of Au₂(dmb)(CN)₂.

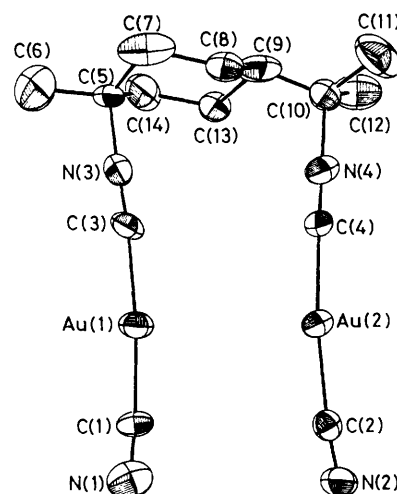| Medium	Emission, λ/nm	Lifetime/ μs at 298 K
Solid	456	0.59
CH_2Cl_2	458	0.13

Figure 1. Perspective drawing and atomic numbering of Au₂(dmb)(CN)₂. Thermal ellipsoids are drawn at 30% probability level. Bond distances (Å): Au(1)–C(1), 1.95(1); Au(1)–C(3), 1.96(1); Au(2)–C(2), 2.00(1); Au(2)–C(4), 1.98(1); N(1)–C(1), 1.10(2); N(3)–C(3), 1.13(2); N(3)–C(5), 1.53(2); N(2)–C(2), 1.11(2); N(4)–C(4), 1.10(2); N(4)–C(10), 1.54(2). Bond angles (°): C(3)–Au(1)–C(1), 173.4(5); C(4)–Au(2)–C(2), 173.5(5); Au(1)–C(1)–N(1), 171(1); Au(1)–C(3)–N(3), 175(1); Au(2)–C(2)–N(2), 170(1); Au(2)–C(4)–N(4), 177(1).
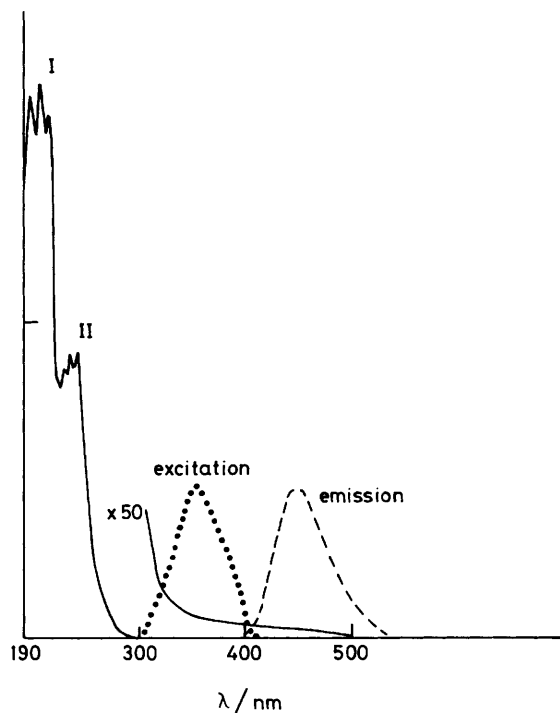
Figure 2. Room temperature u.v.–visible absorption (a), excitation (b), and emission (c) spectra of $Au_2(dmb)(CN)_2$ in CH_2Cl_2.

Excitation of $Au_2(dmb)(CN)_2$ at 250—340 nm in the solid state or in fluid solutions leads to photoluminescene (Table 1). The solid-state emission spectrum is similar to that of solid $K[Au(CN)_2]$,[3c] with a high-energy emission at ~458 nm and a weak, broad, orange emission at 600—700 nm. In fluid solution, only the 458 nm emission is observed (Figure 2). The large Stokes shift between the energies of the 458 nm emission and band II cannot be explained by excited-state distortion and suggests that the 458 nm emission comes from a low-lying spin-forbidden state, which is probably at 338 nm, the excitation λ_{max} of the 458 nm emission (Figure 2).

The observation of a reasonably long-lived (τ_0 is 0.13 μs,

Table 1) and high-energy (~2.8 eV) excited state of $Au_2(dmb)(CN)_2$ in fluid solution indicates the potential rich photochemistry of the binuclear Au^I system. The co-ordinative unsaturated nature of Au^I may facilitate substrate binding, which is important for multi-electron atom-transfer reactions. Recent studies have shown that $Au_2(tmb)(CN)_2$ (tmb = 2,5-dimethyl-2,5-di-isocyanohexane)[12] can be prepared by a similar route, suggesting the possibility of tuning the excited-state properties with variation of the structure of the bridging di-isocyanides.

References

1 (a) S. F. Rice, S. J. Milder, H. B. Gray, R. A. Goldbeck, and D. S. Kliger, *Coord. Chem. Rev.*, 1982, **43**, 349; (b) D. G. Nocera, A. W. Maverick, J. R. Winkler, C. M. Che, and H. B. Gray, *A.C.S. Symp. Series*, 1983, **211**, 21; (c) J. V. Caspar and H. B. Gray, *J. Am. Chem. Soc.*, 1984, **106**, 3029; (d) J. L. Marshall, A. E. Stiegman, and H. B. Gray, *A.C.S. Symp. Series*, 1985, **307**, 166. (e) C. M. Che and W. M. Lee, *J. Chem. Soc., Chem. Commun.*, 1986, 616.
2 See for example, A. P. Zipp, *Coord. Chem. Rev.*, 1988, **84**, 47.
3 (a) W. R. Mason, *J. Am. Chem. Soc.*, 1976, **98**, 5182; (b) S. K. Chastain and W. R. Mason, *Inorg. Chem.*, 1982, **21**, 3717; (c) N. Nagasundaram, G. Roper, J. Biscoe, J. W. Chai, H. H. Patterson, N. Blom, and A. Ludi, *Inorg. Chem.*, 1986, **25**, 2947.
4 (a) J. V. Caspar, *J. Am. Chem. Soc.*, 1985, **107**, 6718; (b) P. D. Harvey and H. B. Gray, *ibid.*, 1988, **110**, 2145.
5 Md. N. J. Khan, J. P. Fackler, Jr., C. King, J. C. Wang, and S. Wang, *Inorg. Chem.*, 1988, **27**, 1672.
6 J. P. Fackler, Jr. and J. D. Basil, *A.C.S. Symp. Series*, 1983, **211**, 201.
7 See for example, F. J. Farsell and T. G. Spiro, *Inorg. Chem.*, 1971, **10**, 1606.
8 A. Rosenzweig and D. T. Cromer, *Acta. Crystallogr.*, 1959, **12**, 709.
9 S. Esperas, *Acta. Chem. Scand., Ser. A.*, 1976, **30**, 527.
10 K. R. Mann, *Cryst. Struct. Commun.*, 1980, **10**, 451.
11 C. M. Che, F. H. Herbstein, W. P. Schaefer, R. E. Marsh, and H. B. Gray, *Inorg. Chem.*, 1984, **23**, 2572.
12 C. M. Che, W. T. Wong, and T. F. Lai, unpublished result.