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Research paper

Photophysics of a mono-nuclear tetrahedral silver(I)N_4 core and its copper(I) analog

Shanti G. Patra [a], Senjuti De [b], Derek A. Tocher [c], Dipankar Datta [a,]*

[a] Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India
[b] Dr. Meghnad Saha College, Ranipur, Tilna, WB 733 128, India
[c] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

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ABSTRACT

A neutral ligand L is prepared by condensation of benzil dihydrazone and acetone in 1:2 mol ratio and used for the syntheses of $[CuL_2]ClO_4$, $[CuL_2]PF_6$, $[AgL_2]ClO_4$ and $[AgL_2]PF_6$. The X-ray crystal structures of L and the two perchlorate salts have been determined. The metal complexes are found to be mononuclear containing tetrahedral N_4 coordination spheres for Cu(I) and Ag(I). Cyclic voltammetrically, the Cu(II/I) and Ag(II/I) potentials are 1.23 and 0.76 V vs NHE respectively in CH_2Cl_2 at a Pt electrode. The reason for the such a low Ag(II/I) potential is that the silver(I) complex is adsorbed on the electrode surface with a free energy of adsorption of ~ -14.99 kcal mol^{-1}. DFT calculations at the BP86/LanL2DZ level show that the HOMO's in $[CuL_2]ClO_4$ and $[AgL_2]ClO_4$ are both metal based and the LUMO's have no contribution from the metals. Both complexes show weak emissions from the MLCT states upon excitation at 270 nm in ethanol solution at room temperature. Changing the counterion to PF_6^- leads to higher quantum yields for these processes. It is consistent with the general observation that ClO_4^- being more coordinating than PF_6^-, it binds the metals in the MLCT state to form exciplexes leading to a lower ϕ or total quenching. At 77 K in ethanol glass, L, $[CuL_2]^+$ and $[AgL_2]^+$ show ligand centered (LC) emissions. Thus the MLCT and LC states are thermally equilibrated in the silver(I) and copper(I) complexes. In keeping with this, a mixture of the two processes, MLCT and LC emissions, is observed at room temperature for $[AgL_2]ClO_4$ and $[CuL_2]ClO_4$ when they are incorporated in a rigid polymethyl methacrylate matrix.

1. Introduction

There is significant current interest in the design of transition metal complexes which can emit throughout the visible region [1–5]. Their potential for applications in optoelectronics is enormous [6–13]. In this regard phosphors of Ir(III), Pt(II) and Os(II) are studied most extensively. Some Ir materials have been standard-setting in the field of organic light emitting devices [14,15]. However these metals are very expensive and of limited availability. Consequently, there has been an imperative to find low-cost alternatives and the coinage metals may fill this requirement [12,16–21]. For example, mononuclear Cu(I) complexes of the type $[Cu(N—N)(P—P)]^+$ where N—N is a 1,4-diimine like 1,10-phenanthroline (phen) and P—P a bidentate phosphine, are found to have emission properties like those of the best Ir(III) complexes [19,22,23]. Here we are concerned with the basics of the photophysics of mononuclear tetrahedral homoleptic Cu(I) and Ag(I) complexes of a 1,4-diazine (L; Chart 1). While examples of mononuclear.

Cu^IN_4 core are abundant, similar complexes of Ag(I) are rare. As such, photophysics of Ag(I) complexes with tetrahedral coordination geometry similar to their Cu(I) analogs has been seldom studied, possibly because of their light sensitivity and limited luminescent properties [18,21,24]. Thus of the numerous reports on emissive silver(I) complexes to date most involve multinuclear compounds usually having an Ag(I)…Ag(I) bond [11,25,26].

2. Results and discussion

Copper(I) complexes of *N*-donor ligands are usually air sensitive mainly because of the low potential for the Cu(II/I) couple. This air sensitivity of the copper(I) complexes has been effectively exploited by many workers to generate interesting copper(I)-dioxygen chemistry [27–29]. Generation of an air stable CuN_4^+ core requires a ligand that can destabilize the corresponding copper(II) species [30,31]. One way of achieving this is to impose a tetrahedral coordination geometry on the copper(II) species, which

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* Corresponding author.
E-mail address: icdd@iacs.res.in (D. Datta).

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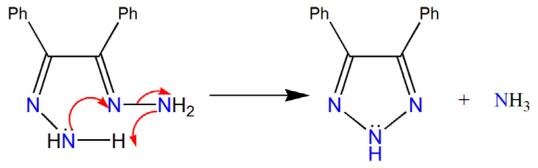
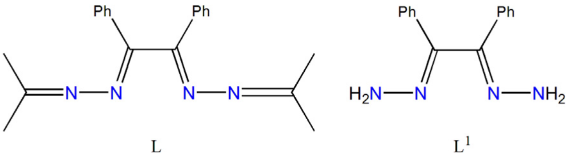


Chart 1. Ligands involved in the present work.

requires carefully designed ligands. We believe benzil dihydrazone (L^1) to be a potential candidate in this regard, as it has a twisted conformation with the torsion angle N=C—C=N of ~70° in the solid state [32].

Reaction of L^1 with $Cu(MeCN)_4ClO_4$ in dry methanol under N_2 in a 2:1 M ratio at room temperature yields an air stable yellow copper(I) complex of the formulation $[Cu(DPT)]ClO_4$ (DPT = 4,5-diphenyl-2*H*-[1,2,3] triazole). A tentative mechanism for the metal-assisted conversion of L^1 to DPT is proposed in Scheme 1 [33]. Our attempts to isolate the organic moiety in $[Cu(DPT)]ClO_4$ in the free state by treating the complex with ammonia have resulted in the isolation of L^1 only.

Realizing that the free NH_2 groups of L^1 are problematic, we have capped them by reaction with acetone, i.e. we have prepared the 1:2 acetone condensate (L) of L^1 which is characterised by X-ray diffraction (Fig. 1). L is observed to adopt a staggered conformation about the C1-C11 bond (C12-C11-C1-C2 = 85.0°, N1-C1-C11-N3 = 90.6°) in order to minimize the steric interactions between the phenyl groups. The C=N bond lengths are all closely similar (1.263(3)-1.279(3) Å) and the *N*—*N* bonds (1.401(3) and 1.403(3) Å) are somewhat shorter than the conventional single bond length (1.46 Å) between a pair of nitrogen atoms due to conjugation. Selected crystal data for L are given in Table 1. Its ^1H NMR spectrum is shown in Fig. S1 as Supplementary material.



Scheme 1.

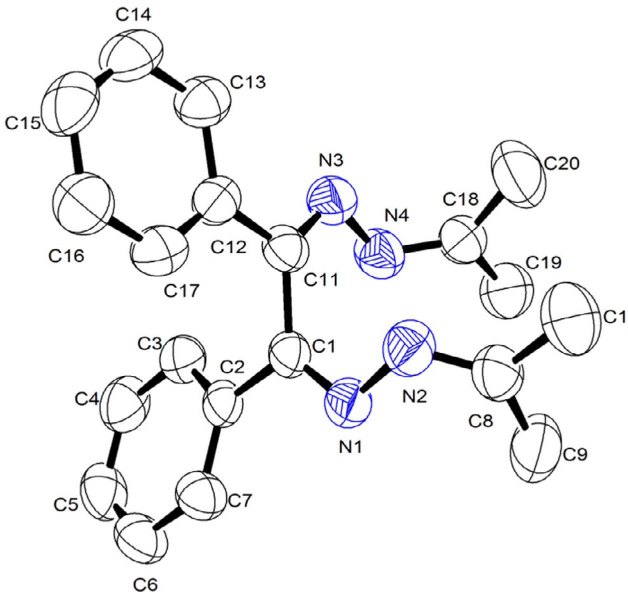


Fig. 1. The molecular structure of L showing the atom numbering scheme (H atoms omitted for clarity and thermal ellipsoids at the 50% probability level). Selected bond lengths (Å) and bond angles (°): N(1)-N(2) 1.403(3), C(18)-C(20) 1.492(4), N(1)-C(1) 1.278(2), N(2)-C(8) 1.269(3), N(3)-N(4) 1.401(3), N(3)-C(11) 1.279(2), N(4)-C(18) 1.264(3), C(1)-C(11) 1.512(3), C(8)-C(9) 1.478(4), C(8)-C(10) 1.499(4), N(2)-N(1)-C(1) 114.44(17), C(12)-C(17)-C(16) 121.5(2), N(1)-N(2)-C(8) 114.79(19), N(4)-C(18)-C19 116.7(2), N4-N3-C11 113.12(17), N4-C18-C20 124.8(2), N3-N4-C18 117.28(19), C(19)-C(18)-C(20) 118.6(2), N(1)-C(1)-C(2) 118.81(17), N(1)-C(1)-C(11) 123.54(17).

Table 1
Selected crystallographic data for L, $[CuL_2]ClO_4$ and $[AgL_2]ClO_4$.

	L	$[CuL_2]ClO_4$	$[AgL_2]ClO_4$
Formula	$C_{20}H_{22}N_4$	$C_{40}H_{44}ClCuN_8O_4$	$C_{40}H_{44}ClAgN_8O_4$
M	318.42	799.82	844.15
Temperature (K)	293(2)	293(2)	150(2)
Crystal System	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*C2*/*c*	$P2_12_12_1$
Cell dimensions (Å, °)			
a	8.3224(6)	22.2164(15)	15.7595(9)
b	18.6230(13)	22.1042(15)	15.7934(9)
c	11.8431(8)	17.2452(12)	16.0104(9)
α	90.00	90.00	90.00
β	95.2700(10)	113.8660(10)	90.00
γ	90.00	90.00	90.00
U ($Å^3$)	1827.8(2)	7744.6(9)	3984.9(4)
Z, d_{calc} ($g\ cm^{-3}$)	4, 1.157	8, 1.372	4,1.407
$\mu(mm^{-1})$	0.070	0.685	0.624
F(0 0 0)	680	3344	1744
Unique reflections	4351	9157	9544
Observed reflections [*I* greater than 2σ (*I*)]	3295	8212	9030
R_{int}	0.0229	0.0252	0.0195
Parameters	217	488	499
R_1, wR_2 [*I* greater than 2σ (*I*)]	0.0748, 0.2097	0.0496, 0.1225	0.0344, 0.0878
R_1, wR_2 (all data)	0.0933, 0.2250	0.0554, 0.1261	0.0366, 0.0893
Largest peak/hole (e $Å^{-3}$)	0.494/-0.154	0.656/-0.401	1.236/-0.500

The reaction of L with copper(II)acetate monohydrate in methanol in 2:1 M ratio and subsequent addition of an excess of $NaClO_4{\cdot}H_2O$ gave yellow crystals of the copper(I) complex $[CuL_2]ClO_4$. The same compound is obtained from the reaction of L with $[Cu(MeCN)_4]ClO_4$ in a 2:1 M ratio in methanol under N_2 atmosphere. The complex crystallizes in the monoclinic space group C2/c with two cations, each located on a two fold axis (therefore only half of each cation is crystallographically unique), and one ordered perchlorate anion in the asymmetric unit. The two cations are essentially identical in all significant aspects of their geometry and one of them is shown in Fig. 2. Selected crystal data for $[CuL_2]ClO_4$ are given in Table 1. The copper is ligated by two bidentate ligands and the geometry about Cu1 is distorted tetrahedral with the four independent angles subtended by the ligating atoms being 95.75(9), 96.81(9) 105.34(7) and 128.76(7)°. The two smaller values are due to the bidentate bite of the two seven-membered chelates. Earlier we have seen that when the phenyl rings of L are replaced by methyl groups, the resulting ligand L' binds Ru(II) in $[Ru(bpy)_2L']^{2+}$ (bpy = 2,2′-bipyridine) in a fashion such that a five-membered chelate ring is generated with smaller bite angle, ~76° [34]. Chelation affects the conformation adopted by L in $[CuL_2]^+$ such that the torsion angles noted in the free ligand are reduced by about 20° (C5-C4-C4A-C4 = 66.0, N2-C4-C4A-N2A = 77.7, C15-C14-C14A-C15A = 71.8, N4-C14-C14A-N4A = 76.3°). The C=N and N—N bond lengths in the coordinated ligands are not significantly different from those observed for the free ligand. The two Cu-N distances in $[CuL_2]^+$ are closely similar (2.049(2) and 2.055(2) Å). The two CuN_2 planes intersect each other at ~72°. Though the unit cell of $[CuL_2]ClO_4$ contains two independent