Synthesis, Structure and Photoluminescent Studies of a Novel Supramolecular [Ag(phen)(CN)]·(phen) Complex

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Keywords: Density functional calculations / N ligands / Pi interactions / Photoluminescence / Silver

A novel Ag^I complex [Ag(phen)(CN)]·(phen) (phen = 1,10-phenanthroline) has been solvothermally synthesized and characterized by X-ray diffraction. The crystal packing reveals unprecedented threefold interpenetrating three-dimensional four-connected networks self-assembled through C-H···N hydrogen bonds and π···π stacking interactions, which are stabilized by strong C-H···π interactions between the three independent networks. The photoluminescent properties have been investigated by molecular orbital (MO) calculations, showing that the luminescent properties of the complex in the solid state are due to both a $\pi_L \rightarrow \pi_L{}^*$ transition of the uncoordinated phen species and metal-to-ligand charge transfer (MLCT), admixed with the cyanide-to-ligand charge transfer (XLCT) of the [Ag(phen)(CN)] species.

Introduction

In the field of crystal engineering, many attempts have been made to control the molecular arrangement in a crystal using hydrogen bonds and π···π stacking interactions. The unique strength and direction of these interactions play important roles in the generation of a variety of molecular architectures.[1−8] Non-conventional hydrogen bonds with weak proton donor C-H groups are of great theoretical interest, especially for C-H···N hydrogen bonding interactions.[9−12] Many novel supramolecular structures have been constructed using these weak interactions, such as the supramolecular graphyne-like network structure of 2,4,6-triethynyl-1,3,5-triazine.[6]

1,10-Phenanthroline (phen) is a suitable ligand to study these supramolecular interactions since it contains a large π-system and rich C−H donors. Various novel structures have been constructed with phen and such interactions in our previous work.[13,14] Phen and its derivatives have also been widely used for synthesizing materials with interesting photoluminescence properties. Over the past two decades the photochemical and photophysical properties of d^{10} metal-phen complexes have been extensively investigated.[15−17] Most reported d^{10} metal-phen complexes are cationic, whereas their neutral complexes are rarely documented.[18] Recently, we have synthesized a variety of neutral d^{10} complexes with an unsymmetrical hydroxylated phen ligand; molecular orbital (MO) calculations of these compounds give an effectual proof in the analysis of their interesting photoluminescent mechanism.[19] Herein we describe the synthesis and crystal structure of a novel molecular adduct of a neutral silver(I) complex with a solvate phen molecule, [Ag(phen)(CN)]·(phen) (**1**), which exhibits interesting supramolecular interactions in the solid state. The photoluminescent properties of complex **1** have been investigated and the mechanisms have also been validated by MO calculations on the experimental geometries.

Results and Discussion

Synthesis and Characterization

Complex **1** was prepared by a solvothermal reaction from silver oxide and excess phen in a concentrated aqueous ammonia and acetonitrile mixture. The existence of a cyanide group in complex **1** may be due to the decomposition of acetonitrile at the relatively high temperature (140 °C) and autogenous pressure of the reaction, which is somewhat similar to the process of acetonitrile decomposition under physiological conditions.[20] The formation of the stable mononuclear species [Ag(phen)(CN)] may be ascribed to the slow release of the cyanide ligand from acetonitrile and the multiple weak interactions between [Ag(phen)(CN)] and excess phen ligand, since direct addition of the cyanide salt usually yielded polymeric products.[21]

The IR spectrum of complex **1** shows one band at 2128 cm^{-1}, which can be assigned to the ν(CN) stretching vibration of the terminal CN^- species, taking into account that it is close to the recorded value for $K[Ag(CN)_2]$ (2140

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DOI: 10.1002/ejic.200300616

cm^{-1}).[22] The ν(CN) stretching vibration for terminally bound CN$^-$ complexes shifts to higher energy than that (2080 cm^{-1})[23] of free cyanide ion in water due to the strong σ donation of the weakly anti-bonding lone pair on CN$^-$ to the metal, but to lower energy than those found for linear M−CN−M complexes such as [Ag$_2$(L^2)$_2$(μ-CN)][BF$_4$] [L^2 = 4,7-bis(2-cyanomethyl)-1-thia-4,7-diazacyclononane] (2150 cm^{-1})[24] where the two metal centres are coupled.

Crystal Structure

The X-ray single-crystal structure analysis shows that complex **1** is a 1:1 molecular adduct of mononuclear [Ag(phen)(CN)] and an uncoordinated phen ligand. The [Ag(phen)(CN)] molecule is bisected by a crystallographic mirror plane. The silver(I) atom assumes a Y-shaped planar geometry in which the metal ion is ligated by two nitrogen atoms of a phen and one carbon atom of the terminal cyanide, as shown in Figure 1. The Ag(1)−N(2) distance is 2.301(2) Å, while the Ag(1)−C(1) bond length is 2.026(5) Å. The observed Ag−N distances are similar to the corresponding values [2.283(6) and 2.300(5) Å] found for Ag(dmp)NO$_3$·2H$_2$O (dmp = 2,9-dimethyl-1,10-phenanthroline),[25] while the Ag−C distance is typical of silver cyanide, and is shorter than that [2.083(2) Å] found for [Ag$_2$(L^2)$_2$(μ-CN)][BF$_4$] [L^2 = 4,7-bis(2-cyanomethyl)-1-thia-4,7-diazacyclononane].[24] In complex **1**, the N(2)−Ag(1)−C(1) bond angle is 143.4(1)°, whereas the N(2)−Ag(1)−N(2A) angle is 73.3(1)°.

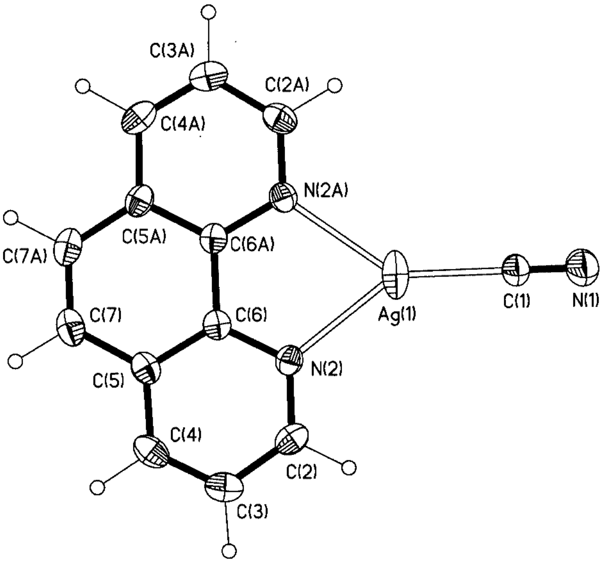

Figure 1. Perspective view of [Ag(phen)(CN)] (30 % thermal ellipsoids) with atom-numbering scheme; selected bond lengths (Å) and bond angles (°): Ag(1)−N(2) 2.301(2); Ag(1)−C(1) 2.026(5); N(2)−Ag(1)−C(1) 143.4(1); N(2)−Ag(1)−N(2A) 73.3(1); symmetry code: A) 1/2 − *x*, *y*, *z*

Cyanometallates are useful building blocks for the construction of supramolecular structures. Such supramolecular assemblies are usually achieved through bridging linear covalent M−CN−M bonding interactions.[23] In contrast, successful attempts to use a cyanide as a terminal ligand, especially for a hydrogen-bond acceptor, are rare.[26] The most intriguing feature in the structure of complex **1** is its unusual supramolecular interactions, including C-H···N hydrogen bonds, π···π stacking and C-H···π interactions involving the terminal cyanide and phen ligands, generating a unique supramolecular architecture in the solid state (Figure 2).

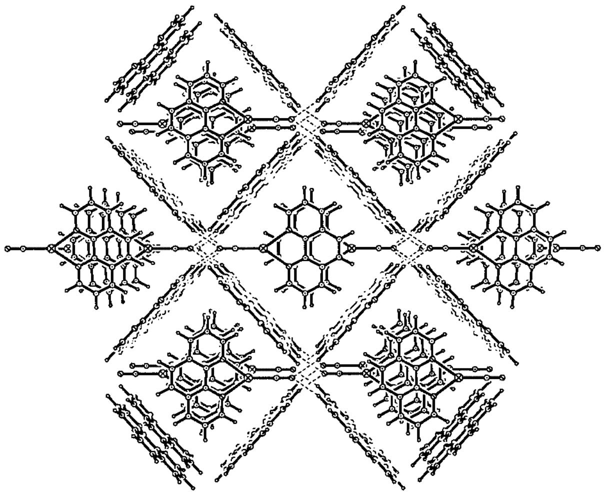

Figure 2. Crystal packing pattern of **1** viewed along the *a* axis

Adjacent [Ag(phen)(CN)] molecules in complex **1** are stacked in an inverse fashion through strong offset π···π aromatic stacking interactions, with a face-to-face distance of about 3.40 Å, forming a one-dimensional array (Figure 3, top),[3] whereas the uncoordinated phen molecules are arranged to give extended one-dimensional ribbons with relatively long C-H···N(phen) contacts (C···N 3.61 Å, H···N 2.60 Å, C-H···N 155°; Figure 3, bottom), where the H···N distance is still shorter than the van der Waals radii sum of 2.75 Å.[27] It is very interesting that the arrays and the ribbons are extended into a novel three-dimensional structure by strong C-H···N(CN) hydrogen bonds (C···N 3.41 Å, H···N 2.35 Å, C-H···N 164.4°). There are a few reported networks built from both weak C-H···X hydrogen bonds and π···π interactions.[13,14,28,29] A noteworthy example is the diamondoid network made up of C-H···O hydrogen bonds and π···π interactions in the structure of tetrakis(4-nitrophenyl)methane·G (G = THF, dioxane, nitrobenzene, 4-bromoanisole, anisole, ethoxybenzene, *p*-xylene, chlorobenzene).[28] The C-H···N hydrogen bonds are consistent with the previous report of this type of interactions, for example, the short C-H···N hydrogen bonds (C···N 3.27 Å, H···N 2.31 Å, C-H···N 180° and C···N 3.30 Å, H···N 2.34 Å, C-H···N 172.1°) in the structure of 2,4,6-triethynyl-1,3,5-triazine.[6] It should be noted that the acidity of C$_{\text{(phen)}}$−H is significantly weaker than C$_{\text{(sp)}}$−H or Cl$_3$C-H, which are involved in the most reported short and linear C-H···N hydrogen bonds.[5]

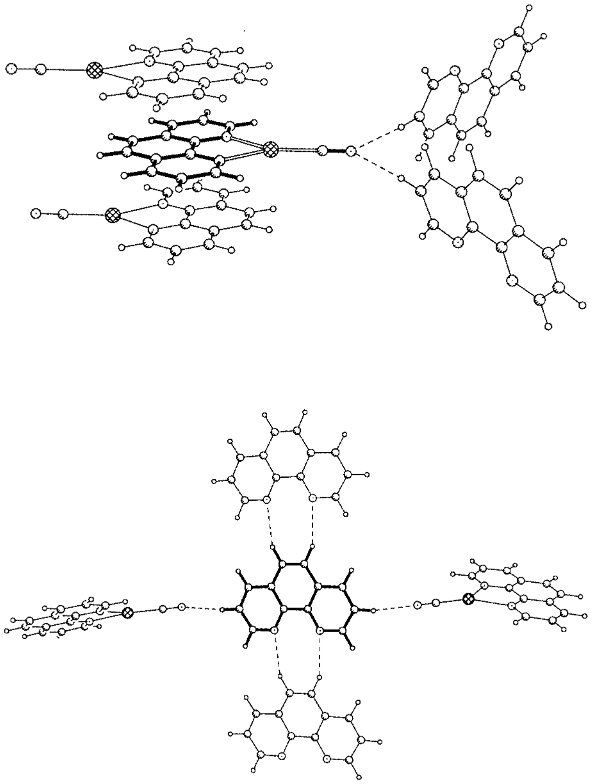

Figure 3. (top) The tetrahedral node defined by an [Ag(phen)(CN)] molecule connected to two other [Ag(phen)(CN)] molecules by π···π stacking interactions and two uncoordinated phen molecules by C-H···N hydrogen bonds; (bottom) the square-planar node defined by an uncoordinated phen molecule connected to two [Ag(phen)(CN)] moieties and two uncoordinated phen molecules by C-H···N hydrogen bonds

As shown in Figure 3, each [Ag(phen)(CN)] molecule forms hydrogen bonds and π···π interactions with its adjacent molecules in a tetrahedral arrangement (Figure 3, top), which can be regarded as a tetrahedral node; each uncoordinated phen molecule forms hydrogen bonds with its adjacent molecules in a square-planar arrangement, which can be regarded as a square-planar node (Figure 3, bottom). The three-dimensional structure of complex **1** linked by hydrogen bonds and π···π interactions can therefore be rationalized to contain equal numbers of tetrahedral nodes and square-planar nodes, where every node is connected to two nodes of the same type and two nodes of the other type (Figure 4, top). The resulting unprecedented binodal four-connected $(5^5 6)(5^4 8^2)$ topology is related to the well-known PtS net since it contains equal numbers of tetrahedral and square-planar nodes. However, the nodes of the PtS net are arranged in such a way that every node is connected to four nodes of the other type, in contrast to the topology found in complex **1**.[30] There is threefold interpenetration, with the networks being linked through edge-to-face C-H···π interactions between the coordinated ligands and uncoordinated phen molecules of the three nets, as illustrated in Figure 4 (bottom). Other examples of interpenetrating three-dimensional hydrogen-bonding networks linked by weak interactions include the structures of 4-(carboxamindo)-1-cubanecarboxylic acid, [Zn(Him)$_2$(tpa)]·H$_2$O (Him = imidazole, tpa = terephthalate) and NH$_4$(bpedo)$_2$PF$_6$·3H$_2$O [bpedo = *trans*-bis(4-pyridyl)ethylene dioxide].[31–33] The pattern of C-H···π hydrogen bonds is very interesting in **1**, as there are two sets of contacts, with the short one having an H···π interaction of about 2.39 Å (C-H···π ca. 163°) and the longer one an H···π interaction of about 2.82 Å (C-H···π ca. 163°), which results in every coordinated phen species containing four C−H donors and every uncoordinated phen species being an acceptor for four C−H donors from two coordinated phen ligands (Figure 5).

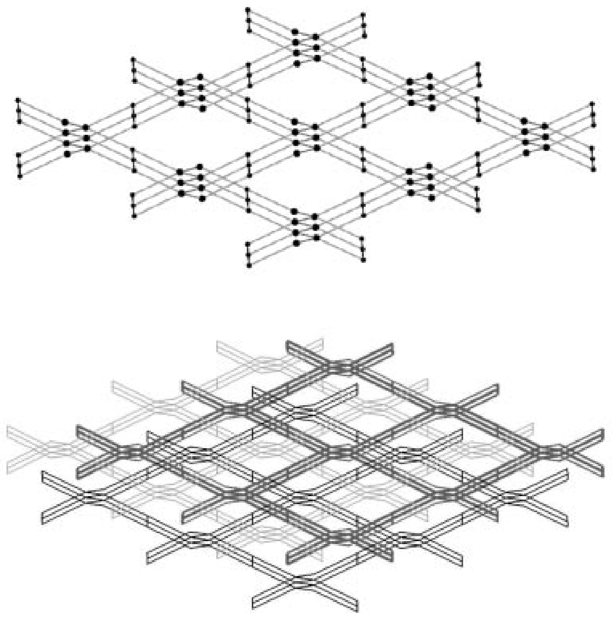

Figure 4. (top) The four-connected net constructed by the tetrahedral ([Ag(phen)(CN)], larger spheres) and square-planar (phen, smaller spheres) nodes, as well as (bottom) the threefold interpenetrating nets in **1**

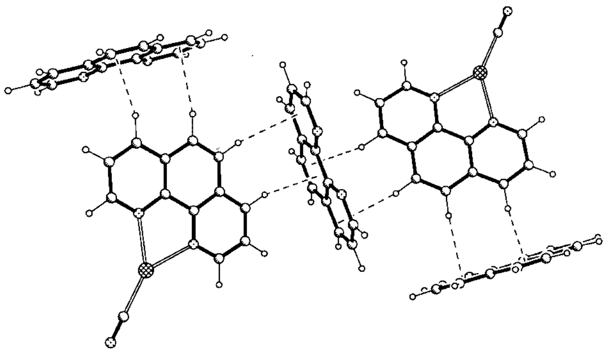

Figure 5. Perspective view of the C-H···π interactions

Luminescent Properties

Most luminescent Ag^I compounds exhibit emission at low temperature. Some important examples are organometallic silver(I) compounds containing bridging acetylide ligands,[34] silver(I) diisocyanide[35] and other silver(I) cyanide compounds.[36] Only a few monomeric and polymeric Ag^I complexes exhibit luminescence at room temperature.[37–41] Interestingly, solid **1** is luminescent at ambient temperature. Upon excitation at 325 nm, complex **1** displays an intense blue photoluminescence with three emission maxima at 406, 420 and 529 nm. The first two emission bands resemble the π-π* transition bands (385 and 403 nm) observed for solid phen (see Figure 6) due to the presence of uncoordinated phen molecules in **1**.

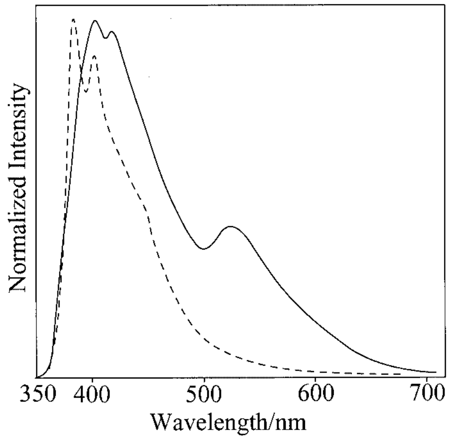

Figure 6. Photoluminescent spectra of solid **1** (−) and phen (---) (excited at 325 nm) in the solid state at room temperature

It has been suggested that the emission bands in the reported silver(I) complexes originate from dσ*-pσ or 4d−5s transitions, the excited states of a metal-to-ligand charge transfer (MLCT), or have an MMLCT character.[42–45] To assign the emission bands, we carried out molecular orbital (MO) calculations on the mononuclear [Ag(phen)(CN)] species and the phen molecule with the experimental geometries. The relevant HOMOs and LUMOs for [Ag(phen)(CN)] and phen, together with the orbital energies, are shown in the contour plots in Figure 7. For uncoordinated phen, the HOMOs are associated with the π-bonding orbital from the phen rings, while the LUMOs are mainly associated with the π-antibonding orbital; for [Ag(phen)(CN)], the HOMOs are mainly composed of σ(Ag−C≡N) orbitals, localized more on the metal center (namely the d_{z^2} orbit), while the LUMOs are mainly composed of the π-antibonding orbital from the phen rings. There are deviations between the HOMO−LUMO analysis derived from our calculations (HOMO−LUMO gaps for [Ag(phen)(CN)] 3.74 eV; for phen 4.84 eV) and the experimentally measured emission energy (ca. 2.34 and 3.10 eV), since only the ground states were taken into consideration in the MO calculations. Moreover, extensive transverse interactions, such as π···π stacking, C−H···π interactions and C−H···N hydrogen bonds, exist in the real solid state and play an essential role in decreasing the HOMO−LUMO gaps.[19,46,47] These supramolecular interactions may also account for the decrease of the HOMO−LUMO gap of the phen groups in complex **1** compared to that of solid phen, resulting in a red-shift of the higher energy emission bands for complex **1**. Moreover, it is worthy to mention that the trend derived from the calculations is in accordance with the experimental results. As a characteristic of large heterocyclic aromatic ligands, the conjugated system can effectively decrease the π*-orbital energies, therefore the LUMO may not be contributed by the metal atom, as demonstrated by the MO calculation results of [Ag(phen)(CN)]. The ligation of a d^{10} metal atom to the heterocyclic aromatic ligand will further decrease the LUMO energy contributed by the π*-orbital, resulting in a much lower-energy emission band for the [Ag(phen)(CN)] species in complex **1**. It can therefore be concluded from the MO calculations that, for the adduct compound **1** in the solid state, the high-energy emission bands can mainly be assigned to the $\pi_L \rightarrow \pi_L^*$ transition of the uncoordinated phen molecules, whereas the low-energy transition is expected to be the metal-to-ligand charge transfer (MLCT), admixed with the cyanide-to-ligand charge transfer (XLCT) band.

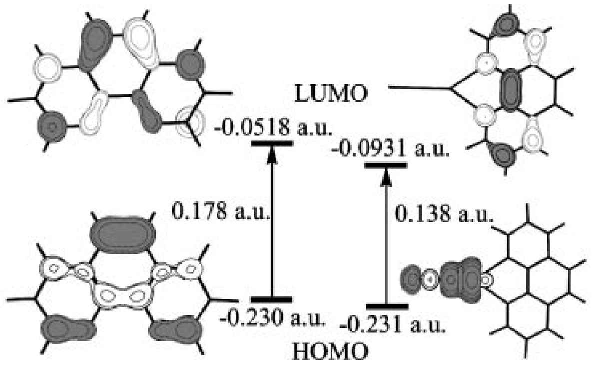

Figure 7. Contour plots and orbital energies of the HOMOs and LUMOs for phen (left) and [Ag(phen)(CN)] (right)

Conclusion

In summary, complex **1** shows an unprecedented four-connected three-dimensional network through cooperative π···π stacking interactions and C-H···N hydrogen bonds; the threefold interpenetrating net is connected by C-H···π interactions between the coordinated phen and uncoordinated phen species. The photoluminescence mechanism of **1** has been studied by molecular orbital calculations, showing that the photoluminescent properties are due to both the $\pi_L \rightarrow \pi_L^*$ transition of the uncoordinated phen molecule and metal-to-ligand charge transfer (MLCT), admixed with the cyanide-to-ligand charge transfer (XLCT) of the [Ag(phen)(CN)] molecule.

Experimental Section

General Remarks: The reagents and solvents employed are commercially available and were used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin−Elmer 240 elemental analyser. The FT-IR spectra were recorded from KBr pellets in the range 4000−400 cm^{-1} on a Nicolet Magna 750 FT-IR spectrometer. The emission spectra were recorded on a Perkin−Elmer LS50B fluorescence spectrophotometer, and the excitation source used was the 325 nm line of He-Cd laser (Kimmon IK5352R-D) with maximum power of 4 mW.

Synthesis of [Ag(phen)(CN)]·(phen) (1): Single crystals of complex **1** were obtained by a solvothermal method. In a typical procedure, silver oxide (0.5 mmol, 0.116 g), phen (2 mmol, 0.400 g), concentrated aqueous ammonia (5 mL) and acetonitrile (5 mL) were mixed sufficiently with stirring and placed into a 25-mL Teflon-lined steel autoclave and heated at 140 °C for 72 h, then cooled to 5 °C/h to 80 °C and held at that temperature for 10 h, followed by slow cooling to room temperature. Pale-yellow crystals (0.101 g) were collected in 20 % yield based on Ag_2O. $C_{25}H_{16}AgN_5$ (494.30): calcd. C 60.75, H 3.26, N 14.17; found C 60.43, H 3.78, N 14.15. FT-IR (KBr): $\tilde{\nu}$ = 3415 cm^{-1} (br. s), 3044 (m), 2925 (m), 2128 (m), 1683 (w), 1646 (m), 1618 (m), 1565 (m), 1503 (s), 1417 (s), 1136 (m), 1091 (m), 837 (m), 792 (w), 723 (m), 621 (w), 461 (w), 433 (w).

X-ray Crystallographic Study: A pale-yellow crystal ($0.40 \times 0.30 \times 0.30$ mm^3) of complex **1** suitable for X-ray analysis was selected and data collection was performed at 21 °C on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using the SADABS program.[48] The structure was solved by direct methods and refined with full-matrix least-squares technique using the SHELXTL software suite.[49] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically with a restricted bond length (C−H 1.083 Å). The crystallographic data are listed in Table 1. CCDC-216802 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal and structure refinement for complex **1**

Empirical formula	$C_{25}H_{16}AgN_5$
Molecular mass	494.30
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
space group	Pnna
a (Å)	7.186(1)
b (Å)	18.599(4)
c (Å)	15.177(3)
V (Å^3)	2028.4(7)
Z	4
Calculated density (Mg/m^3)	1.619
Absorption coefficient (mm^{-1})	1.017
F(000)	992
Crystal size	$0.40 \times 0.30 \times 0.30$ mm^3
θ range for data collection (°)	1.73 to 26.00
Limiting indices	$-8 \le h \le 8$, $-22 \le k \le 17$, $-17 \le l \le 18$
Reflections collected/unique	10063/1990 [R_{int} = 0.033]
Completeness to θ = 26.00°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7502 and 0.6866
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1990/0/143
Goodness-of-fit on F^2	1.068
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0410, wR_2 = 0.1004
R indices (all data)	R_1 = 0.0542, wR_2 = 0.1079
Extinction coefficient	0.0005(4)
Largest diff. peak and hole (e·Å^{-3})	0.380 and −0.425

Calculational Details: Density functional calculations were performed with the Gaussian 98 suite of programs,[50] at the B3LYP level. The basis set used for C, O, N and H atoms was 6−31G while effective core potentials with a LanL2DZ basis set were employed for transition metals. The contour plots of MOs were obtained with the Molden 3.5 graphic program.[51]

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20001008), the Ministry of Education of China (key project grant 01134) and a Doctorate Program Fund (No. 20020558024). The authors thank Prof. Kang-Cheng Zheng for his help in the MO calculations.

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Received September 2, 2003
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