Reexamination of the Photophysical Behavior of Complexes of Iridium(III) Containing Phenanthroline Ligands

R. Ballardini,*[1a] G. Varani,[1a] L. Moggi,[1b] and V. Balzani[1b]

Istituto Chimico dell'Università, Centro di Studio sulla Fotochimica e
Reattività degli Stati Eccitati dei Composti di Coordinazione,
Ferrara, Italy, and Istituto Chimico "G. Ciamician" dell'Università, Bologna, Italy.
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Abstract: We have reexamined the photophysical behavior of *cis*-Ir(phen)$_2$Cl$_2$$^+$ and *cis*-Ir(Me$_2$phen)$_2$Cl$_2$$^+$ (phen = 1,10-phenanthroline; Me$_2$ = 5,6-dimethyl) which were reported to exhibit emission from two different excited states and exciplex formation with naphthalene. It is shown that one of the two emissions and the exciplex formation are due to very small amounts of by-products which are very difficult to eliminate. Absorption spectra, emission spectra, and emission lifetimes of really pure samples of the two complexes are reported.

In the last few years many papers have appeared on the luminescence of Ru(II), Rh(III), Os(II), and Ir(III) complexes containing 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or their derivatives as ligands. Excellent investigations on the photophysical behavior of these complexes at low temperature have been carried out by Crosby's[2] and DeArmond's[3] groups. The luminescence emission of these complexes is present even in fluid solution at room temperature, a very precious property for monitoring the interaction between the excited state and other molecules. This is one reason why these complexes (particularly, Ru(bpy)$_3$$^{2+}$) are extensively used for energy[4] and electron[5-7] transfer processes.

The luminescence emission of these metal chelates is generally thought to originate from the lowest spin-forbidden excited state, whose orbital nature may be π-π^*, d-π^*, or d-d, depending on the metal and ligands involved.[8] The orbital and spin labels, however, may actually lose much of their meaning owing to configuration interaction[9,10] and spin-orbit coupling.[11]

The Ir(III) complexes of bpy and phen are generally more difficult to obtain than the analogous Ru(II), Rh(III), and Os(II) complexes. Ir(bpy)$_3$$^{3+}$ and Ir(phen)$_3$$^{3+}$ have only been prepared and characterized very recently,[12,13] whereas the previously reported[14-18] tris-chelates have in fact been shown to be *cis*-Ir(AA)$_2$X$_2$$^+$ species (X = halogen).[19] Furthermore, the compound reported as *trans*-[Ir(phen)$_2$Cl$_2$]Cl[16] is actually (phenH)[Ir(phen)Cl$_4$].[19,20]

The *cis*-Ir(phen)$_2$Cl$_2$$^+$ and *cis*-Ir(Me$_2$phen)$_2$Cl$_2$$^+$ complexes (Me$_2$phen = 5,6-dimethyl-1,10-phenanthroline), which are the object of the present work, can be prepared by a variety of methods.[14-17,19,21-23] In the last few years, several photophysical[2,3,8-11,18,24-33] and photochemical[22,29,34-36] investigations have been carried out on these complexes and some peculiar properties have been evidenced, such as solvent effects on the photophysical parameters,[10,26] formation of exciplexes,[28] and, very recently, dual emission from excited states of different orbital nature.[30,33] This last property is rather unusual not only for transition metal complexes but also for organic molecules (Kasha rule[37,38]). In the chemical literature there are several examples of dual emissions first attributed to two different excited states of the same molecule and then shown to be caused by impurities, chemical equilibria, or environmental effects. Therefore, we decided to reexamine the photophysical behavior of these complexes in order to obtain more information on their peculiar properties. The results obtained in this work show that both the dual emission[30,33] and the formation of exciplexes with naphthalene[28] are in fact due to the presence of some impurities that are extremely difficult to eliminate.

Experimental Section

Materials. *cis*-Dichlorobis(1,10-phenanthroline)iridium(III) chloride trihydrate, [Ir(phen)$_2$Cl$_2$]Cl·3H$_2$O, can be prepared by different routes: (i) fusion of phenanthroline and K$_3$IrCl$_6$ or (NH$_4$)$_2$IrCl$_6$ in a sealed tube;[14-16,19,21] (ii) refluxing phenanthroline and (NH$_4$)$_3$IrCl$_6$ in water on dimethylformamide (DMF) for very very long time periods;[17,21] (iii) heating (phenH)[Ir(phen)Cl$_4$] in glycerol for 1 min at 290 °C.[22,23,30] In all cases a mixture of compounds is obtained. Purification is usually performed by recrystallization and/or column chromatography. We have prepared a sample of [Ir(phen)$_2$Cl$_2$]Cl·3H$_2$O by method (iii) following the indications given by Broomhead and Grumley[22] and Watts et al.[30] Hereafter, the sample so obtained will be called sample A. Its elemental analysis gave the following result: Calcd for C$_{24}$H$_{22}$N$_4$Cl$_3$O$_3$Ir: C, 40.43; H, 3.11; N, 7.86; Cl, 14.92; Ir, 26.96. Found: C, 40.35; H, 3.14; N, 8.00; Cl, 15.10; Ir, 27.05.

Repeated recrystallizations of sample A from water or acidic water with addition of KCl did not cause any further purification of the sample. On the contrary, recrystallization of sample A from methanol (followed by washing with methanol and ether and air drying) caused the emission spectrum of the compound to undergo progressive changes which will be explained in detail under Results. After 5-6 recrystallizations, a sample was obtained (about 1 g, from 3 g of sample A) whose emission spectrum did not undergo appreciable changes upon further recrystallization. Hereafter, this sample will be called sample B. The results of its elemental analysis are: C, 40.33; H, 3.21; N, 7.91; Cl, 14.83; Ir, 26.81.

A portion of sample B was dissolved in glycerol and heated at 290 °C, i.e., at the temperature used in the synthesis of the compound.[22] The solution was then subjected to the subsequent steps of the preparation method.[22] The product obtained in this way will be called sample C.

Samples A and B of *cis*-dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) chloride trihydrate, [Ir(Me$_2$phen)$_2$Cl$_2$]Cl·3H$_2$O, were prepared following the same procedures indicated above for the analogous samples of the previous complex. Anal. Calcd for C$_{28}$H$_{30}$N$_4$Cl$_3$O$_3$Ir: C, 43.73; H, 3.93; N, 7.28; Cl, 13.83; Ir, 24.99. Found: For sample A, C, 41.62; H, 4.24; N, 6.77; Cl, 13.46; Ir, 23.64. For sample B, C, 43.54; H, 4.04; N, 7.19; Cl, 13.98; Ir, 24.77. A sample spectroscopically identical to sample B was also obtained after 12 recrystallizations of sample A from water or acidic water.

Repeated concentrations of the mother liquors of sample B of Ir(phen)$_2$Cl$_2$$^+$ finally yielded about 0.5 g of a *reddish solid* whose elemental analysis was: C, 47.91; H, 4.38; N, 9.52; Cl, 12.30; Ir, 21.67. Such values roughly correspond to C$_{36}$H$_{39}$N$_6$Cl$_3$O$_2$Ir, indicating that the solid contains iridium and phenanthroline approximately in the 1:3 ratio and that some phenanthroline is partially hydrogenated.

The solvents used in the spectrofluorimetric measurements were

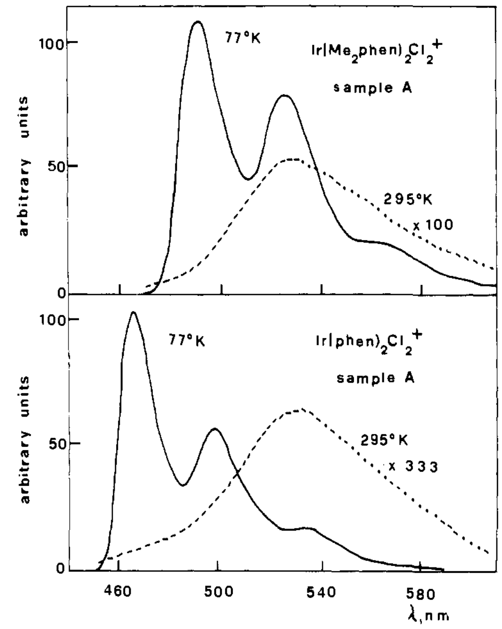

Figure 1. Emission spectra of samples A of Ir(phen)$_2$Cl$_2$$^+$ and Ir(Me$_2$phen)$_2$Cl$_2$$^+$ in glycerol (λ_{exc} 337 nm).

of spectrophotometric grade and the other chemicals were of reagent grade.

Apparatus. Uncorrected emission and excitation spectra were performed with a Perkin-Elmer MPF-3 spectrofluorimeter, using a R-106 photomultiplier tube. The response of this tube decreases less than three times in going from 460 to 560 nm, so that it does not cause substantial changes in the shape of the emission spectra in the wavelength region examined. Emission lifetimes were measured by means of a modified Applied Photophysics apparatus which is based on the single photon counting technique. The solutions were irradiated at 337 nm with a thyratron gated air flash lamp (repetition rate 20 kHz). The pulses had a full-width at half-height of 3.1 ns. Both exciting and emitted light beams were filtered by means of grating monochromators. The performance of the single photon counting equipment was checked by measuring the emission lifetime of rhodamine B; the value of 3.3 ns measured with this apparatus is in good agreement with the literature value of 3.2 ns.[39] Deaeration was accomplished by the bubbling of pure nitrogen for 30 min. Absorption spectra were recorded by means of a Perkin-Elmer 323 spectrophotometer. Continuous photolysis experiments were carried out as previously described.[29] Thin-layer chromatography on Baker-flex Aluminium oxide IB-F was performed using ethanol for elution. Elemental analyses were performed by the Bernhardt Mikroanalytisches Laboratorium, Elbach, Germany.

Results

Samples A. The properties of samples A of the two complexes were as follows:

(i) **Thin-layer chromatography:** no indication of impurities or by-products.

(ii) **Absorption spectra:** essentially identical with those shown in ref 29 for water and 95% v/v DMF-water solutions (see also ref 19 and 36).

(iii) **Emission spectra:** in glycerol at 77 and 295 K (Figure 1), the emission spectra were very similar to those reported by Watts et al.[30] Note that the emission intensity is much higher at 77 K than at room temperature. In DMF at 77 K, the spectra were like those in glycerol at the same temperature. In water and 95% v/v DMF-water, the spectra were practically identical with those reported in ref 29.

(iv) **Excitation spectra (DMF solutions, room temperature):** noticeably different when they were monitored in the maximum (490 nm for Ir(phen)$_2$Cl$_2$$^+$, 495 nm for Ir(Me$_2$phen)$_2Cl_2$$^+$) or in the tail (580 nm) of the emission band.

(v) **Emission quenching by oxygen (DMF solutions, room temperature):** much bigger in the tail than in the maximum of the emission band.

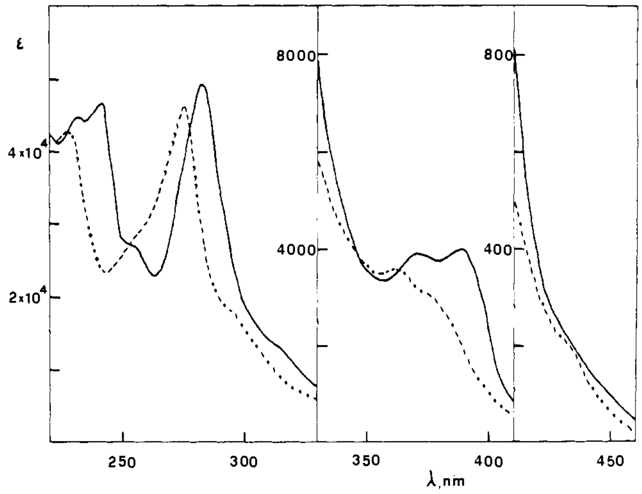

Figure 2. Absorption spectra of samples B of Ir(phen)$_2$Cl$_2$$^+$ (- - -) and Ir(Me$_2$phen)$_2$Cl$_2$$^+$ (—) in water.

(vi) **Luminescence decay (deaerated DMF solutions, room temperature):** slightly nonexponential; approximate lifetimes were 300 ns when monitored at 480 nm and 210 ns at 560 nm for Ir(phen)$_2$Cl$_2$$^+$, and 600 ns at 495 nm and 500 ns at 560 nm for Ir(Me$_2$phen)$_2$Cl$_2$$^+$.

(vii) **Addition of naphthalene (DMF solutions, room temperature):** quenching of the luminescence emission and appearance of a new broad band around 560 nm, as we had previously reported.[28]

(viii) **Photosensitivity:** spectral variations as those described in ref 29 in 10^{-3} M NaOH solution; very small spectral changes in DMF solution.

Samples B. The emission spectra in aerated and deaerated DMF solutions at room temperature were recorded for each sample obtained by successive recrystallization of sample A from methanol. Recrystallization was found to increase the I_{max}/I_{580} ratio (where I_{max} and I_{580} are the intensities in the maximum and in the tail of the emission band) and to decrease the I_d/I_a ratio (where I_d and I_a are the emission intensities of deaerated and aerated solutions at the same wavelength). The changes in the I_{max}/I_{580} ratio were more pronounced for deaerated solutions and those in the I_d/I_a ratio for the tail of the emission band. The spectral changes became smaller and smaller with increasing number of recrystallizations and were no longer appreciable after 5-6 recrystallizations (sample B).

The properties of samples B of the two complexes were as follows:

(i) **Thin-layer chromatography:** no indication of impurities or by-products.

(ii) **Absorption spectra (Figure 2):** practically identical with those of samples A as far as the UV region is concerned; somewhat lower extinction coefficients in the visible region (e.g., 20% around 450 nm).

(iii) **Emission spectra:** in glycerol (Figure 3), the spectra at 77 K were essentially identical with those of samples A (Figure 1), but no emission was observed at 273 and 295 K. In DMF, at 77 K the spectra were again identical with those of samples A, whereas at room temperature the emission of samples B was somewhat lower than that of samples A in the tail of the emission band (Figure 4). For both complexes we have also recorded the spectra at 77 K in 1:1 glycerol-ethanol and 1:1 glycerol-water, and we have found that, as previously reported by Watts et al.,[10,26] the energy of the Ir(Me$_2$phen)$_2$Cl$_2$$^+$ emission is solvent independent, whereas for Ir(phen)$_2$Cl$_2$$^+$ there is a blue shift with increasing polarity of the solvent.

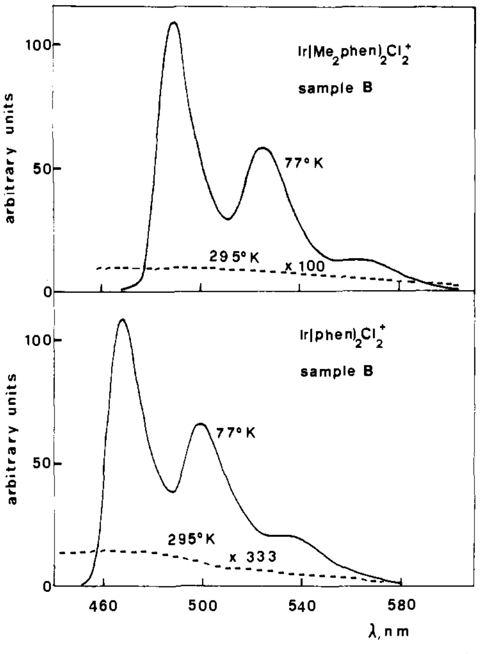

Figure 3. Emission spectra of samples B of Ir(phen)$_2$Cl$_2^+$ and Ir(Me$_2$phen)$_2$Cl$_2^+$ in glycerol (λ_{exc} 337 nm). The spectra at 273 K are substantially identical with those at 295 K.

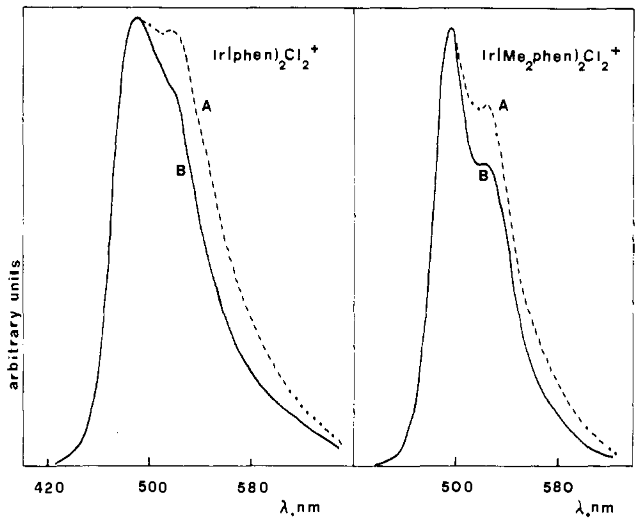

Figure 4. Emission spectra of samples A and B of Ir(phen)$_2$Cl$_2^+$ and Ir(Me$_2$phen)$_2$Cl$_2^+$ in DMF deaerated solutions at room temperature (λ_{exc} 400 nm).

(iv) **Excitation spectra (DMF solutions, room temperature)**: independent of the monitoring wavelength.

(v) **Emission quenching by oxygen (DMF solutions, room temperature)**: equal effect in the maximum and in the tail of the emission band.

(vi) **Luminescence decay (deaerated DMF solutions, room temperature)**: the luminescence decay was exponential, with lifetime 310 ns for Ir(phen)$_2$Cl$_2^+$ and 860 ns for Ir(Me$_2$phen)$_2$Cl$_2^+$, independent of the monitoring wavelength. In deaerated acetonitrile solutions at room temperature, the lifetime was 325 ns for Ir(phen)$_2$Cl$_2^+$ and 915 ns for Ir(Me$_2$phen)$_2$Cl$_2^+$.

(vii) **Addition of naphthalene (DMF solutions, room temperature)**: quenching of the luminescence emission without appearance of new bands.

(viii) **Photosensitivity**: practically identical with that of samples A.

Sample C. The sample C of Ir(phen)$_2$Cl$_2^+$ gave results very similar to those obtained with sample A as far as emission and excitation spectra, quenching by oxygen, and addition of naphthalene are concerned.

Reddish Solid. The reddish solid obtained from the mother liquors of sample B of Ir(phen)$_2$Cl$_2^+$ exhibited an absorption spectrum similar to those of samples A and B in the UV region but noticeable higher in the visible. The emission spectrum, in DMF solution at room temperature, shows a broad, intense band around 530 nm.

Discussion

The comparison between the properties of samples A (i.e., compounds prepared and purified according to the procedure described in the literature[22,30]) and samples B (which are obtained from samples A by successive recrystallizations controlled by emission spectroscopy) shows that samples A contain some impurities which play an important role in the photophysical behavior at high temperatures. Specifically, these impurities are responsible for the broad emission band observed in glycerol at 295 K (Figure 1), for the high intensity of the tail of the emission band in DMF solution at room temperature (Figure 4), for the nonexponential luminescence decay, for the wavelength dependence of the lifetime, and for the growth of a new emission band upon naphthalene addition.

As the elemental analyses of samples A (impure) and B (pure) are essentially identical (at least for Ir(phen)$_2$Cl$_2^+$),[40] the impurities present in samples A must have very small concentrations, unless they have stoichiometric compositions very similar to those of the *cis*-[Ir(AA)$_2$Cl$_2$]Cl·3H$_2$O complexes. The trans isomers, *trans*-[Ir(AA)$_2$Cl$_2$]Cl·3H$_2$O, and the aquo substitution products, [Ir(AA)$_2$Cl(H$_2$O)]Cl$_2$·2H$_2$O and [Ir(AA)$_2$(H$_2$O)$_2$]Cl$_3$·H$_2$O, satisfy this last requirement, but the trans isomers are unknown[41] and the aquo products, owing to their higher positive charge, should have been easily separated in the column chromatography procedure used in the preparation.[42] In the case of Ir(phen)$_2$Cl$_2^+$, we estimate from emission intensity measurements that the impurity which is responsible for the 530-nm emission in glycerol solution at room temperature is at least 25 times less concentrated in sample B than in sample A and about 8 times more concentrated in the reddish solid than in sample A.

The results obtained with sample C of Ir(phen)$_2$Cl$_2^+$ suggest that the impurities are by-products which are formed during the preparation of the complexes because of the drastic conditions (heating at 290 °C in glycerol) used. The elemental analysis of the reddish compound obtained from the mother liquors of sample B seems to indicate that these by-products contain species derived from reactions between phenanthroline rings.[43]

In conclusion, our results show that the dual emission[30] and the formation of exciplexes with naphthalene[28] previously observed for samples of Ir(phen)$_2$Cl$_2^+$ and Ir(Me$_2$phen)$_2$Cl$_2^+$ prepared and purified following the literature method[22,30] are due to very small amounts of by-products. These by-products, however, do not substantially affect the photophysical behavior at 77 K, because under these conditions their emissions are completely hidden by the more intense emission of the "pure" complexes. As far as the photochemical behavior is concerned, it seems plausible that the presence of very small amounts of impurities did not substantially affect the results previously reported.[29]

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(40) The slight difference between the elemental analyses of samples A and B of Ir(Me$_2$phen)$_2$Cl$_2^+$ may correspond to the presence of five (instead of three) water molecules in sample A.
(41) In spite of considerable efforts by several laboratories, no *trans*-M(phen)$_2$X$_2$ complex has yet been obtained. See, for example, M. P. Hancock, J. Josephsen, and C. E. Schäffer, *Acta Chem. Scand., Ser. A*, **30**, 79 (1976).
(42) Another reason for discarding the aquo products is that their luminescence emission is weaker than that of the Ir(AA)$_2$Cl$_2^+$ complexes.
(43) A reddish compound which exhibits an emission band around 500 nm is also produced by heating phenanthroline alone in glycerol at 290 °C. This compound was found to behave as the complexes during the chromatographic elution.

Absence of Metal Interaction with Sulfur in Two Metal Complexes of a Cysteine Derivative. The Structural Characterization of Bis(*S*-methyl-L-cysteinato)cadmium(II) and Bis(*S*-methyl-L-cysteinato)zinc(II)

Patrice de Meester and Derek J. Hodgson*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514.

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Abstract: The complexes bis(*S*-methyl-L-cysteinato)cadmium(II) (Cd(SMC)$_2$, $C_8H_{16}CdN_2O_4S_2$) and bis(*S*-methyl-L-cysteinato)zinc(II) (Zn(SMC)$_2$, $C_8H_{16}ZnN_2O_4S_2$) have been synthesized and their crystal structures have been determined from three-dimensional single-crystal x-ray counter data. The complex Cd(SMC)$_2$ crystallizes in the monoclinic space group $P2_1$ with two formula units in a cell of dimensions $a = 13.314$ (9), $b = 5.074$ (4), $c = 9.839$ (7) Å and $\beta = 96.34$ (4)°. Full-matrix least-squares refinement has reached an R factor (on F) of 0.052 for 913 independent reflections with $F^2 > 2\sigma(F^2)$. The complex is a polymer extending approximately in the crystallographic b-c plane. Two SMC ligands coordinate to the cadmium atom through N(amino) and O(carboxylate) with bonds ranging from 2.26 (1) to 2.28 (2) Å. The slightly distorted octahedral geometry at the metal atom is completed by two carboxylate oxygen atoms of neighboring ligands, at longer distances Cd-O of 2.46 (1) and 2.47 (2) Å. This complex has a structure very similar to that of bis(L-methioninato)cadmium(II). The complex Zn(SMC)$_2$ is also monoclinic, space group $P2_1$ with a cell of dimensions $a = 13.433$ (12), $b = 5.323$ (4), $c = 9.603$ (8) Å and $\beta = 107.52$ (3)° with two formula units per cell. Full-matrix least-squares refinement has reached $R = 0.059$ (on F) using 1330 independent reflections with $F^2 > 2\sigma(F^2)$. The Zn(SMC)$_2$ complex, which is not isostructural with Cd(SMC)$_2$, consists of infinite chains centered about a twofold screw axis parallel to b. The zinc atoms have the less usual trigonal-bipyramidal geometry with three Zn-O(carboxylate) bonds [1.980 (7) to 2.125 (6) Å] and two Zn-N(amino) bonds of 2.035 (7) and 2.087 (9) Å. One of the two SMC ligands coordinates to the metal via its two carboxylate oxygen atoms and its amino nitrogen atom, while the other SMC ligand donates only one carboxylate oxygen atom and its amino nitrogen atom.

Introduction

The role of sulfur-containing ligands, such as BAL (2,3-dimercaptopropanol),[1] 2,3-dimercaptosuccinic acid,[2] and derivatives of cysteine like penicillamine (β,β-dimethylcysteine) and *N*-acetylpenicillamine, is currently being investigated in several laboratories in order to have a better understanding of their potential therapeutic action against toxic heavy metal ions.[3-6] A definite body of single-crystal determinations of such metal complexes is now available and has led to more direct information concerning the nature and extent of metal bonding. Cysteine or its derivatives present three