Ternary Complexes of Copper(I) with 2,9-Dimethyl-1,10-phenanthroline and some Oxygen-donor Ligands

By Whei-Lu Kwik and Kok-Peng Ang,* Department of Chemistry, National University of Singapore, Bukit Timah Road, Singapore 1025

A series of eight ternary complexes, viz. [Cu(dmphen)L] (dmphen = 2,9-dimethyl-1,10-phenanthroline, L = a bidentate oxygen-donor ligand), has been synthesised and characterised. In those complexes containing a β-diketonate, substitution of CF_3 for CH_3 of the acetylacetonate is accompanied by a shift of the C–O and C–C stretching vibrations to higher frequencies and that of the M–O to lower frequencies, indicative of the strong positive inductive effect of the CF_3 group. The ^1H n.m.r. spectral results indicate that the eight ternary systems, unlike [Cu(dmphen)$_2$Cl], remain essentially undissociated in chloroform solution.

TERNARY complexes of copper(II) containing an α,α'-di-imine as the primary ligand and an oxygen-donor ligand as the secondary one have aroused a considerable amount of interest in recent years. This is to be attributed to the unusual stabilities of these complexes as demonstrated by extensive solution studies [1-4] as well as to their suitability to serve as models for enzyme–metal ion–substrate complexes. In addition many of these complexes have been isolated as solids and their bonding characteristics fairly thoroughly studied by u.v.–visible, i.r., e.s.r., and polarographic as well as conductivity measurements.[5-7]

As many copper-containing proteins are involved in redox reactions [8] the corresponding copper(I) ternary complexes are, therefore, of biological significance. This is particularly so as it has been established that the composition of the active site of such proteins is governed by the stringent requirement that electron transfer is to occur without ligand displacement. Furthermore with appropriately chosen oxygen-donor ligands, such copper(I) complexes, once formed, readily allow probing of the nature of the extent of the interaction between copper(I) and the oxygen atom of the selected ligands. Such interaction has assumed new biological significance following recent findings from spectroscopic studies [9] that the copper(II)–transferrin interaction is likely to involve the copper ion and the phenolate oxygen. Thus a study of the copper(I) ternary systems may contribute to a better understanding of the biochemical significances of copper.

In relation to the formation of Cu^I–α,α'-di-imine complexes, the 2,9-dimethyl-1,10-phenanthroline (dmphen) ligand is of particular interest for the following reasons: (a) it has been established that dmphen stabilises Cu^I over Cu^{II} to such an extent that the species [Cu(dmphen)]$^{2+}$ becomes a strong oxidising agent; (b) the mono species, [Cu(dmphen)]$^+$, can be formed preferentially over the bis form, [Cu(dmphen)$_2$]$^+$, by maintaining a sufficiently large excess of copper(I) ion in solution. This, in turn, would facilitate the formation of the corresponding ternary complexes; and (c) the resulting ternary complexes containing dmphen could be expected to possess significantly higher solubilities in common organic solvents than those of the unsubstituted α,α'-di-imines. Such enhanced solubilities

would render the ternary systems more amenable to various physiochemical methods of studies including the n.m.r. technique.

We now report the synthesis and investigation of a series of ternary complexes of copper(I) containing dmphen as well as one of the following oxygen-donor ligands: acetylacetonate (acac), trifluoroacetylacetonate (tfacac), thenoyltrifluoroacetylacetonate (ttacac), hexafluoroacetylacetonate (hfacac), acetate, oxalate (HC$_2$O$_4$), malonate (Hmal), and succinate (Hsucc). The bonding characteristics of these complexes are investigated through i.r. spectral, electronic spectral, conductivity, and ^1H n.m.r. spectral measurements.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer model 567 spectrometer which was calibrated with polystyrene film; KBr pellets and Nujol mulls were employed throughout. Solid-state electronic spectra were obtained by mounting the Nujol mull on filter paper, while the solution spectra were run at a concentration of approximately 10^{-3} mol dm^{-3} using a Hitachi 124 spectrometer. The ^1H n.m.r. spectra were recorded at 90 MHz on a Perkin-Elmer R32 spectrometer.

All chemicals used were of AnalaR grade. Solvents were purified and dried by the usual methods.

Preparation of Complexes.—Freshly prepared copper(I) chloride (0.54 g) in dry acetonitrile (20 cm³) was slowly added to a near boiling solution of 2,9-dimethyl-1,10-phenanthroline (0.40 g) in ethanol (20 cm³), and heated under reflux for 1 h till a clear red solution was obtained. As this solution was being heated and stirred magnetically, an ethanolic solution of the dicarboxylic acid or the β-diketonate of equimolar quantity to dmphen was slowly added. The pH of the resultant mixture was adjusted to ca. 6.0 with alcoholic ammonium hydroxide and the mixture allowed to reflux over an oil-bath for 24 h. An intensely red solution was obtained which was filtered and then evaporated to dryness under reduced pressure in an atmosphere of nitrogen.† The intense red solid so obtained was recrystallised twice from a mixed solvent of benzene–absolute alcohol (10 : 1).

† Preliminary investigations on the variation of the absorbance of these complexes in solution as oxygen was bubbled through appear to indicate that molecular oxygen reacts with these complexes in a partially reversible manner. Systematic studies on this aspect are in progress.

TABLE 1

Microanalytical and conductivity data

	Found (%)				Calc. (%)				Λ_m/S
Ternary complexes	C	H	N	Cu	C	H	N	Cu	cm² mol⁻¹
[Cu(dmphen)(O₂CMe)]·0.5C₆H₆	61.3	5.0	7.3	16.8	61.7	4.9	7.7	17.2	52
[Cu(dmphen)(HC₂O₄)]·C₆H₆	60.2	5.1	6.6	14.9	60.2	4.7	6.4	14.5	38
[Cu(dmphen)(Hmal)]·0.5C₆H₆	58.7	4.2	7.2	14.8	58.1	4.4	6.9	15.4	54
[Cu(dmphen)(Hsucc)]·2H₂O	52.7	5.2	6.2	14.9	52.3	4.8	6.4	14.6	46
[Cu(dmphen)(acac)]·H₂O	57.8	5.1	7.0	16.7	58.5	5.4	7.2	16.4	55
[Cu(dmphen)(tfacac)]·C₆H₆	58.2	4.6	6.1	11.6	58.6	4.5	5.7	12.6	54
[Cu(dmphen)(ttacac)]·0.5C₆H₆	57.4	4.7	5.1	11.2	57.2	4.3	5.1	11.7	56
[Cu(dmphen)(hfacac)]·1.5H₂O	45.4	3.9	6.2	12.2	45.1	3.5	5.9	12.7	54

RESULTS AND DISCUSSION

Synthetic, Microanalysis, and Solution Studies.—The mono and bis copper(I) complexes, [Cu(dmphen)Cl] and [Cu(dmphen)₂Cl], as reported by Plowman and co-workers,[10] were obtained by reducing the corresponding copper(II) complexes. For the present series of copper(I) ternary complexes we have found that preparations starting from the copper(II) complexes invariably resulted in samples of copper(I) complexes mixed with various amounts of the copper(II) species; subsequent purification was rendered difficult because of the high solubilities of not only the copper(II) but also the copper(I) complexes in common organic solvents such as chloroform, acetone, methanol, and ethanol. It was, however, found that if freshly generated copper(I) chloride was allowed to react with dmphen in a 3 : 1 molar ratio followed by addition of a stoicheiometric amount of the oxygen-donor ligand, the reaction mixture on being refluxed for 24 h yielded almost exclusively the desired copper(I) ternary complexes. Because of the extremely high solubility of the copper(I) complexes in the mixed solvent of ethanol–acetonitrile, which was used throughout the preparations, the solvents had to be removed by evaporation under a stream of nitrogen. The product thus obtained was recrystallised twice from a benzene–absolute alcohol mixture (10 : 1).

Microanalytical results of the isolated copper(I) ternary complexes are given in Table 1. For several of these ternary complexes benzene molecules were present, probably incorporated into the crystal lattice. These solvate molecules could partially be removed upon heating under reduced pressure; however, complete removal of these solvent molecules could not be achieved. This

phenomenon has, in fact, been found [11] to be common among other copper(I) compounds.

The stoicheiometry of these ternary complexes in chloroform solution was established by Job's method of continuous variation,[12] in which solutions of [Cu(dmphen)Cl] and the oxygen-donor ligand were mixed such that the mole fraction of one of the reactants was varied from 0.1 to 0.9 while the total volume as well as the total concentration of the two reactants were kept constant. In each case, plots of the absorbances at three different wavelengths (400, 440, and 450 nm) against the mole fractions were approximately symmetrical and showed maxima at the mol ratio of 1 : 1.

Infrared Spectral Studies.—The i.r. spectra of the copper(I) ternary complexes as well as those of [Cu(dmphen)Cl] and [Cu(dmphen)₂Cl] were measured over the range 200—4 000 cm⁻¹. In the spectra of [Cu(dmphen)(Hsucc)], [Cu(dmphen)(acac)], and [Cu(dmphen) (hfacac)] broad absorption bands are observed around 3 400—3 500 cm⁻¹, indicative of the presence of water molecules. Tentative assignments of the absorption peaks due to: (a) the co-ordinated dmphen; (b) the carboxylate ion; (c) the –C=C– and C=O of the β-diketones; and (d) the Cu^I–N and Cu^I–O stretchings are set out in Table 2.

On comparison of the i.r. spectra of [Cu(dmphen)Cl] and [Cu(dmphen)₂Cl] complexes, it will be noted that the co-ordinated dmphen exhibits different i.r. absorption patterns in these complexes with peaks at (i) 1 620, 1 580, 1 510, 1 435, 870, 845, 775, and 735 cm⁻¹ for [Cu(dmphen)Cl] and (ii) 1 680, 1 630, 1 510, 1 440, 870, 852, 784, and 735 cm⁻¹ for [Cu(dmphen)₂Cl]. It should be clear from Table 2 that absorption patterns of the

TABLE 2

Selected i.r. and far-i.r. absorptions (cm⁻¹) and probable assignments ^{a}

dmphen	[Cu(dmphen)₂-Cl]	[Cu(dmphen)-Cl]	[Cu(dmphen)-(O₂CMe)]	[Cu(dmphen)-(HC₂O₄)]	[Cu(dmphen)-(Hmal)]	[Cu(dmphen)-(Hsucc)]	[Cu(dmphen)-(acac)]	[Cu(dmphen)-(tfacac)]	[Cu(dmphen)-(ttacac)]	[Cu(dmphen)-(hfacac)]	Probable assignments
	1 680w										dmphen
1 660s,s		1 630w									dmphen dmphen
1 610s,s		1 620s,w	1 620s,w	1 615s,w	1 615s,w	1 615s,w	1 610s,w	1 610s,w	1 610s,w	1 610s,w	dmphen
1 580s,s		1 580s,s	1 585s,s	1 575s,s	1 580s,s	1 580s,s	1 580s,s	1 580s,s	1 580s,s	1 580s,s	dmphen
1 520s,s	1 510s,s	1 510s,s	1 508s,s	1 510s,s	1 510s,s	1 510s,s	1 500s,m	1 500s,m	1 500s,m	1 500s,m	dmphen
1 420s,m	1 440s,m	1 435br,s	1 430br,s	1 430br,m	1 430br,m	1 430br,m	1 430s,m	1 430s,m	1 430s,m	1 430s,m	dmphen
	870s,vs	870s,vs	870s,m	865s,s	870s,s	870s,s	865s,s	865s,s	870s,s	860s,s	dmphen
845s,vs	852s,vs	845s,m	845s,m	850s,m	850s,m	850s,m	845s,w	842s,m	845s,s	842s,s	dmphen
780s,m	784s,m	775s,vs	775s,m	775s,w	775s,w	770s,w	767s,w	775s,w	775s,w	770s,w	dmphen
735s,vs	735s,s	735s,vs	735s,s	735s,s	730s,s	730s,s	730s,s	730s,s	735s,s	730s,s	dmphen
				1 720s,s	1 710s,s	1 720s,s					free unionised O–C=O ^{b}
					1 690s,s	1 680s,s					$\nu_{asym.}$(O–C=O)
			1 560s,s	1 580s,s	1 575s,s	1 580s,s					$\nu_{sym.}$(O–C=O)
			1 395s,s	1 405s,s	1 400s,s	1 410s,s					
			237w	228s,w	230s,w		1 580s,s	1 615s,s	1 620s,s	1 660s,s	ν(C=C) ^{c}
			278w	280s,s	280s,s		1 550s,s	1 590s,s	1 600s,s	1 610s,s	ν(C=O) ^{c}
						230w	235w	225w	215w	215w	ν(Cu–O)
						282s,s	284m	284m	285m	285m	ν(Cu–N)

^{a} First letters following the frequencies denote sharp (s) or broad (br); others (w, m, s, vs) are intensities. ^{b} Carboxyl. ^{c} β-Diketonate.

dmphen in the ternary complexes show closer similarity to the one in [Cu(dmphen)Cl] than that in [Cu(dmphen)₂-Cl]. This observation would be in line with the fact that the complexes isolated in the present study are actually ternary in character and hence could be formulated as [Cu(dmphen)L] rather than the ionic type, [Cu(dmphen)₂][CuL₂].

Among the ternary complexes formed from acetic, oxalic, malonic, and succinic acids, strong absorption peaks around 1 690—1 720 cm⁻¹ characteristic of a free, unionised carboxyl group [13] (1 700—1 750 cm⁻¹) are detectable for all but the acetate. This would seem to indicate that one of the two carboxyl groups in each of the three dicarboxylic acids remains unco-ordinated in these complexes. Furthermore, absorption frequencies at 1 620 cm⁻¹ and 1 400 cm⁻¹ are probably due to the asymmetric ($\nu_{asym.}$) and symmetric ($\nu_{sym.}$) stretching of the bound carboxylate groups, since these are comparable to those reported for co-ordinated carboxylate groups.[13,14] Vohra and co-workers [15] have suggested that $\Delta\nu$ ($\nu_{asym.} - \nu_{sym.}$) of the ionised unidentate carboxylate group would exceed that of the corresponding sodium salt by ca. 30 cm⁻¹ while the $\Delta\nu$ value of a carboxylate group behaving as a bidentate ligand is approximately equal to that of its sodium salt. The $\nu_{sym.}$ and $\nu_{asym.}$ values for the ternary complexes containing HC₂O₄, Hmal, or Hsucc, are found to be ca. 1 570 and 1 400 cm⁻¹ respectively, leading to a $\Delta\nu$ value of ca. 170 cm⁻¹. This $\Delta\nu$ value when compared to that of sodium acetate ($\Delta\nu$ 164 cm⁻¹) [16] would seem to indicate that the bound carboxylate groups act as bidentate ligands in each of these dicarboxylic acids.

It is interesting to note that whereas in the series of copper(II) ternary complexes reported earlier [6] both carboxyl groups are probably involved in bonding to the metal centre, only one of such groups is co-ordinated in these copper(I) complexes. This may well be due to steric factors, as a tetrahedral configuration is preferred by Cuᴵ in a four-co-ordinate environment.

For complexes containing a β-diketonate ion as the second ligand, the stretching frequencies due to C⋯O and C⋯C are of particular interest as these have been shown by Nakamoto et al.[17] to be markedly affected by substitution of the methyl protons by other groups. Thus, substitution of CF₃ for CH₃ is said to shift the C⋯O and C⋯C stretching to significantly higher frequencies while that of M-O is shifted to lower frequency. This result has been interpreted as an indication of the strong positive inductive effect of the CF₃ group which strengthens the former two bonds but weakens the M-O bond. Our results (Table 2) appear to support this interpretation as the stretching frequencies of the C⋯O and C⋯C bonds increase in going from L = acac through L = tfacac and ttacac to hfacac.

Assignments of the absorption bands in the far-i.r. spectra are rendered difficult as there are only few reports [18-20] on stretching frequencies of ν(Cuᴵ-N) and ν(Cuᴵ-O). Thus, the assignments of ν(Cu-O) and ν(Cu-N) (Table 2) for these complexes are only tentative

and are arrived at after careful comparison and consideration of the reported values for several copper(I) complexes.[18-20] The values for the Cu-O stretching frequencies in complexes containing a β-diketonate follow the expected trend as discussed earlier. However, those due to ν(Cu-N) seem to be relatively insensitive to the nature of the substituents on the methyl groups.

Electronic Spectral and Conductivity Measurement Studies.—The eight copper(I) ternary complexes in chloroform are characterised by an intense ($\varepsilon = 3$—4 × 10³ dm³ mol⁻¹ cm⁻¹) absorption band around 460 ± 5 nm which presumably is due to copper→ligand π* transitions.[21] In addition, a shoulder of approximately half the absorption intensity as that at 460 nm is observed around 380 nm. These absorption maxima remain almost unchanged when the solvent is changed from chloroform to methanol. The solid-state spectra in Nujol show a much broadened absorption band at ca. 470 nm.
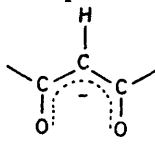
Conductivity results in nitromethane are indicative of ions but somewhat lower than the values expected for a 1 : 1 electrolyte. However, all the ternary complexes are non-conducting in methanol. These results suggest that the complexes undergo solvent-dependent dissociation in solution. Such dissociation has actually been noted in various studies of solution behaviour of many discrete copper(I)–phosphine complexes.[22-25]

Hydrogen-1 N.M.R. Spectral Study.—The ¹H n.m.r. spectra of dmphen show very sharp resonance peaks at δ 7.38, 7.48, 7.62, 8.02, and 8.10 p.p.m. assignable to the protons of the aromatic rings; in addition a single sharp peak due to the protons of the two methyl groups is observed at δ 2.92 p.p.m. The ratio of the integrated area of the multiplet centred at δ 7.74 p.p.m. over that of the single peak is found to be consistent with this assignment. In the [Cu(dmphen)₂Cl] complex, the resonance peaks due to the aromatic rings coalesce to give an ill resolved multiplet at δ 7.98 p.p.m. while that of the methyl protons splits into two sharp peaks. This observed change in the ¹H n.m.r. spectrum in going from the free ligand to the bis complex most probably results from the dissociation of [Cu(dmphen)₂Cl] in chloroform to give [Cu(dmphen)Cl] and dmphen; evidence for such dissociation was first obtained from a spectrophotometric study.[26]

In contrast, within the series of ternary complexes the resonance peaks of both the aromatic as well as the methyl protons of the co-ordinated dmphen remain sharp but are shifted significantly. The fine structure of the aromatic protons together with the sharpness of the peaks in the spectra of all the ternary complexes demonstrate that the concentration of Cuᴵᴵ in these ternary complexes is negligible;[27] moreover unlike [Cu(dmphen)₂Cl], these ternary complexes probably remain largely undissociated in chloroform.

A close examination of the chemical shifts as set out in Table 3 reveals that even though all resonance peaks due to the dmphen are appreciably affected upon complexation, the magnitude of the shifts falls within a

TABLE 3

Hydrogen-1 n.m.r. spectra (δ/p.p.m.) in CDCl₃

β-Diketone
α proton

Complexes/ Unco-ordinated ligand	dmphen		β-Diketone α proton	Other resonances
	Aromatic protons [a]	Methyl protons		
dmphen	7.74	2.92		
[Cu(dmphen)₂Cl]	7.98	2.75, 2.44		
[Cu(dmphen)(O₂CMe)]	8.30	2.45		2.45 [b] (CH₃ of acetate)
[Cu(dmphen)(HC₂O₄)]	8.20	2.45		
[Cu(dmphen)(Hmal)]	8.15	2.45		3.15 (methylene protons of malonic acid)
[Cu(dmphen)(Hsucc)]	8.25	2.42		2.42 (methylene protons of succinic acid)
[Cu(dmphen)(acac)]	8.16	2.42	5.50	2.14 (methyl protons of acac)
[Cu(dmphen)(tfacac)]	8.16	2.45	5.90	2.16 (methyl protons of tfacac)
[Cu(dmphen)(hfacac)]	8.20	2.50	6.10	
[Cu(dmphen)(ttacac)]	8.20	2.45	6.40	

[a] This is obtained by taking the average of the benzene peaks. [b] This is derived from integration of the area of the broad peak which consists of proton peaks of the methyl groups of dmphen as well as those of the acetate.

narrow range for the aromatic protons and is remarkably similar for the methyl protons. The near independence of the shifts on the nature of the oxygen-donor ligands with regard to ring sizes and ability to form delocalised systems could conceivably be attributed to the fact that such effects would be largely attenuated before reaching the immediate environment of the ring as well as the methyl protons.

Within the series of ternary complexes containing a β-diketonate, the δ values of the α proton are comparable to those reported [28] for diamagnetic complexes. It is noted that the shifts upon complexation are only moderate in all cases. For [Cu(dmphen)(acac)] and [Cu(dmphen)(tfacac)] the methyl protons are observed at δ 2.14 and 2.16 p.p.m. respectively.

A single sharp resonance signal assignable to the methylene protons occurs at δ 3.20 p.p.m. for the unco-ordinated malonic acid and at δ 3.15 p.p.m. for the ternary complex. The corresponding signal for those of succinic acid appears at δ 2.65 p.p.m. for the free acid but in the complex it is shown by integration of area to have overlapped with that of the methyl protons of dmphen at δ 2.42 p.p.m. The highly symmetrical form of the latter peak appears to indicate that the unionised, unco-ordinated carboxyl group of succinic acid does not interact to any significant extent with the copper(I) centre. In view of their similar structures the free carboxyl group of malonic acid would be expected to behave in a parallel manner.

[0/963 *Received, 23rd June, 1980*]

REFERENCES

[1] H. Sigel and D. B. McCormick, *Acc. Chem. Res.*, 1970, **3**, 201.
[2] G. A. L'Heureux and A. E. Martell, *J. Inorg. Nucl. Chem.*, 1966, **28**, 481.
[3] R. Griesser and H. Sigel, *Inorg. Chem.*, 1970, **9**, 1238.
[4] H. Sigel, P. R. Huber, R. Griesser, and B. Prij, *Inorg. Chem.*, 1973, **12**, 1198.
[5] F. A. Walker, H. Sigel, and D. B. McCormick, *Inorg. Chem.*, 1972, **11**, 2756.
[6] W. L. Kwik and K. P. Ang, *Aust. J. Chem.*, 1978, **31**, 459.
[7] W. L. Kwik, K. P. Ang, and G. Chen, *J. Inorg. Nucl. Chem.*, 1980, **42**, 303.
[8] R. Malkin and Bo. G. Malmström, *Adv. Enzymol. Relat. Subj. Biochem.*, 1970, **33**, 177.
[9] A. Garnier and L. Tosi, *J. Inorg. Biochem.*, 1979, **10**, 147.
[10] J. R. Hall, N. K. Marchant, and R. A. Plowman, *Aust. J. Chem.*, 1962, **16**, 34.
[11] M. A. S. Goher, *Can. J. Chem.*, 1975, **53**, 2657.
[12] S. Chaberak and A. E. Martell, ' Organic Sequestering Agents,' John Wiley, New York, 1959.
[13] D. H. Busch and J. C. Bailar, *J. Am. Chem. Soc.*, 1956, **78**, 716; K. Swaminathan and D. H. Busch, *J. Inorg. Nucl. Chem.*, 1961, **20**, 159.
[14] R. E. Sievers and J. C. Bailar, *Inorg. Chem.*, 1962, **1**, 174.
[15] B. Hammond, F. H. Jardine, and A. G. Vohra, *J. Inorg. Nucl. Chem.*, 1971, **33**, 1017.
[16] D. A. Edwards and R. N. Hayward, *Can. J. Chem.*, 1968, **46**, 3443.
[17] K. Nakamoto, Y. Morimotto, and A. E. Martell, *J. Phys. Chem.*, 1962, **66**, 346.
[18] H. M. J. Hendriks and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1979, **98**, 95.
[19] A. J. Carty and A. Ifraty, *Inorg. Chem.*, 1969, **8**, 543.
[20] B. W. Cook, R. G. J. Miller, and P. F. Todd, *J. Organomet. Chem.*, 1969, **19**, 421.
[21] B. R. James, M. Parrier, and R. J. P. Williams, *J. Chem. Soc.*, 1961, 4360.
[22] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.
[23] D. A. Edwards and R. Richards, *J. Chem. Soc., Dalton Trans.*, 1975, 637.
[24] E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, 1970, **92**, 4114.
[25] S. J. Lippard and J. J. Mayerle, *Inorg. Chem.*, 1972, **11**, 753.
[26] J. R. Hall, N. K. Marchant, and R. A. Plowman, *Aust. J. Chem.*, 1962, **16**, 480.
[27] P. A. Temussi and A. Vitagliano, *J. Am. Chem. Soc.*, 1975, **97**, 1572.
[28] R. A. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, 1958, **80**, 5658.