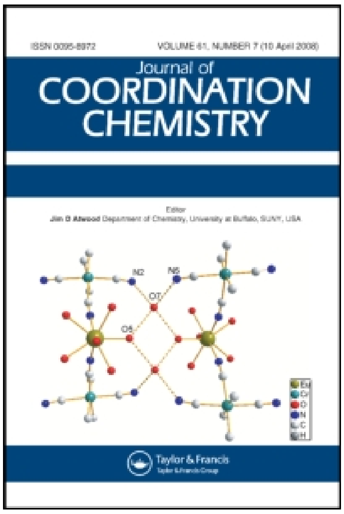

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

NOVEL COMPLEXES OF ANTIPYRINE LIGANDS: DINUCLEAR COPPER(II), COBALT(II) AND NICKEL(II) COMPLEXES OF *N,N'*-TETRA(4-ANTIPYRYLMETHYL)-1,2-DIAMINOETHANE

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To cite this Article Costisor, Otilia , Linert, Wolfgang , Deusch, Stefan and Stanescu, Claudia(1994) 'NOVEL COMPLEXES OF ANTIPYRINE LIGANDS: DINUCLEAR COPPER(II), COBALT(II) AND NICKEL(II) COMPLEXES OF *N,N'*-TETRA(4-ANTIPYRYLMETHYL)-1,2-DIAMINOETHANE', Journal of Coordination Chemistry, 33: 3, 229 — 234
To link to this Article: DOI: 10.1080/00958979408024281
URL: http://dx.doi.org/10.1080/00958979408024281

J. Coord. Chem., 1994, Vol 33, pp. 229–234
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NOTE

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(Received March 10, 1994)

The synthesis and properties of new cobalt, nickel and copper complexes of general formula $M_2(TAMEN)Cl_4$ [M = Co, Ni, Cu; TAMEN = *N,N,'*-tetra(4-antipyrylmethyl)-1,2-diaminoethane; antipyryl- = 2,3-dimethyl-1-phenyl-3-pyrazoline-5-one] and the ^{1}H-NMR spectrum of the ligand TAMEN are reported. TAMEN bridges the two metal centres *via* two groups of donor atoms, each being formed of the carbonylic oxygens and a 1,2-diaminoethane nitrogen atom.

KEYWORDS: antipyrine, synthesis, characterization, polynuclear complexes

INTRODUCTION

Antipyrine compounds have been reported to show anti-tumor and anti-pyretic properties,[1–3] and these properties might be influenced by complex formation. This led us to the preparation and characterization of some first row metal complexes with *N,N'*-bis(antipyrylmethyl)piperazine (AMP) as bridging ligand.[4–7] Similarly, *N,N'*-tetra(4-antipyrylmethyl)-1,2-diaminoethane (TAMEN) has six potential coordination sites, but steric considerations permit it to function only as a double-terdentate ligand. Two groups of donor atoms each consisting of two carbonylic oxygen atoms and a 1,2-diaminoethane nitrogen atom may coordinate. The present paper is concerned with investigations of changes in coordination and chelating abilities of TAMEN where structural particularities of the complexes have been the main point of interest.

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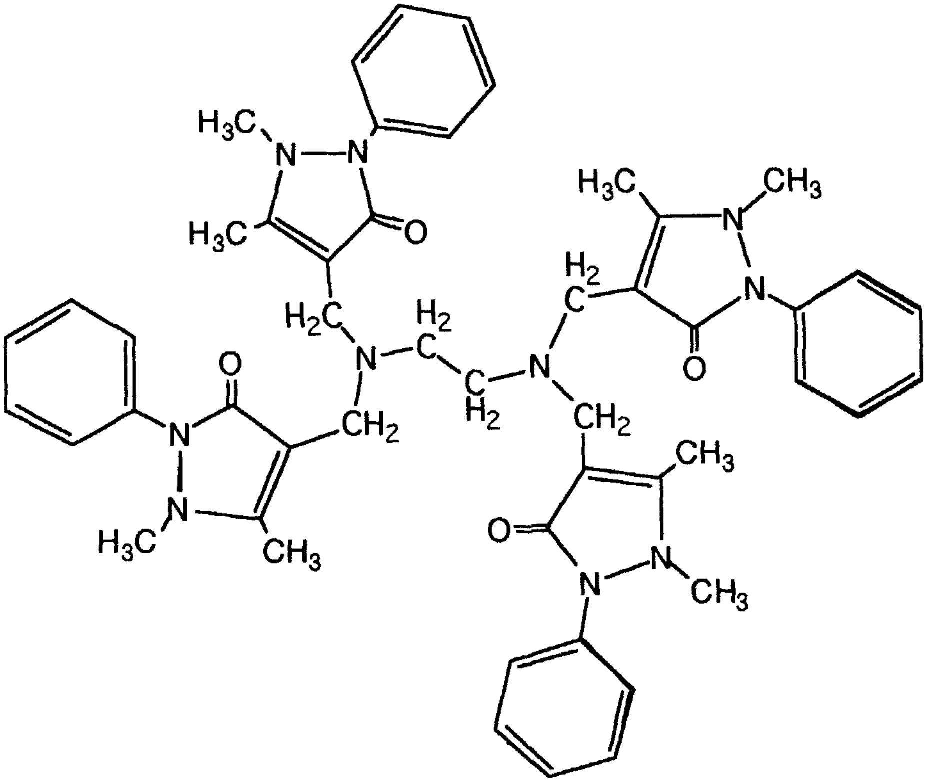


Scheme 1 Two dimensional constitutional isomer of TAMEN [tetra(4-antipyrylmethyl)-1,2-diaminoethane].

EXPERIMENTAL

Synthesis

TAMEN was obtained by a Mannich reaction from antipyrine with ethylenediamine in an aqueous formaldehyde solution as published earlier.[5]

$M_2(TAMEN)Cl_4$, where M = Co, Cu, Ni: 10 mmol of MCl_2 in water:ethanol = 1:1 was treated with 5 mmol TAMEN dissolved in 15 cm^3 of ethanol with stirring. After 15 to 20 minutes the complexes precipitated as blue microcrystalline powders. The complexes were purified by recrystallisation from ethanol and dried in air over P_2O_5. By slow evaporation of an aqueous solution of $Ni_2(TAMEN)Cl_4$ single crystals were obtained.

Physical Measurements

Electric conductivities were measured in DMF solution with a Radelkis conductometer. Magnetic susceptibilities were determined by the Gouy method at 20°C using $Hg[Co(CNS)_4]$ as calibrant. Diamagnetic corrections for the ligands were made. IR spectra in KBr pellets were recorded on a Perkin-Elmer 16PC FT-IR spectrometer (600–4000 cm^{-1}). Far infrared spectra of the compounds in a polyethylene matrix were measured on a Nicolet 20F FT-IR spectrometer (650–150 cm^{-1}). Electronic absorption spectra of KBr pallets and of freshly prepared Nujol suspensions were measured with a Hitachi U-2000 spectrophotometer. ^1H-NMR spectra of the free ligand TAMEN were recorded on a 250 MHz Bruker spectrometer relative to TMS in DMSO-d_6 as solvent.

RESULTS AND DISCUSSION

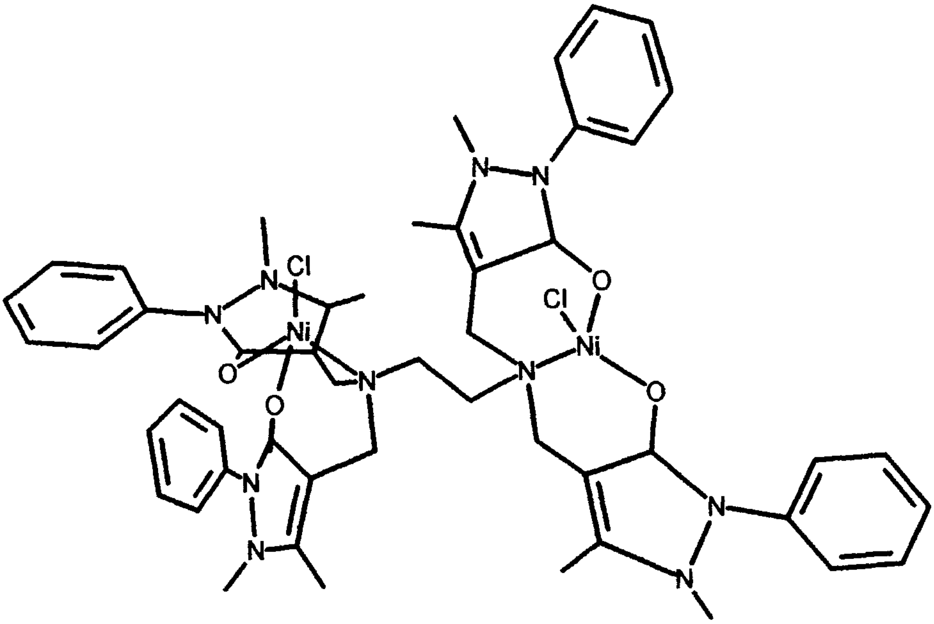
Complexes obtained are listed in Table 1. The homodinuclear complexes were obtained as microcrystalline powders. Variation of the metal to ligand ratio (1:1, 2:1, and 3:1), always yielded the same complex compounds, as confirmed by elemental analysis. This shows that the ligand TAMEN may function only as a double-terdentate ligand and not as a hexadentate (Scheme 1). The proposed structure of the monodinuclear metal complex is shown in Scheme 2.

The ^1H-NMR spectrum of the pure ligand, TAMEN, gave the following shifts in ppm relative to TMS: ^1H-NMR (δ| shape | No. of H) = (7,4| t|8H), (7,2|m|12H), (3,1 | s| 8H), (3,0| s| 12H), (2,6| d | 4H), (2,1 |s | 12H); [s = singlet, t = triplet, m = multiplet]. ^1H-NMR spectra of the metal complex compounds did not yield assignable signals due to the strong paramagnetic coupling of the protons with the metal. For the copper complex all except two peaks of the TAMEN ligand shifted out of the usual 0–10 ppm range due to paramagnetic coupling. Molar conductivities show that at least half the halide ions are able to dissociate in DMSO solutions (Table 1), thus indicating 1:2 electrolyte behaviour per metal centre. Electronic absorption data are presented in Table 2. In the spectrum of $Cu_2(TAMEN)Cl_4$ in nujol a large band at 658 nm appears. The band is strongly shifted in solution to longer wavelength and seems to be solvatochromic, *i.e.*, the shift is more pronounced in the stronger donor solvent DMSO than in DMF. However, the spectra show that the metal coordination centers are in a tetrahedral environment.[9] Obviously the bulkiness of the substituents prevent six-coordination of metals. According to this, dinuclear species should be present in solution. In spectra of the Cu complex a large and very intense band at about 430 nm appears, which, according to its position and intensity, could be a charge transfer band.

In agreement with the literature[10] we assign the observed band in the spectrum of (2) at 633 nm to a $^4A_2$ to $^4T_1$ (P) transition which is characteristic for the Co^{2+} ion in a C_{2v} pseudotetrahedral surrounding. Its fine structure is a result of spinorbit

Table 1 Elemental analyses (calculated values in parentheses), magnetic moments (μ) and molar conductivity in DMSO solutions (Λ_c) of the investigated complexes at a concentration of 10^{-4} M.

Compound	Elemental Analyses/%					μ/μ_{BM}	$\Lambda_c/\Omega^{-1}mol^{-1}cm^2$
	H	C	N	Cl	metal		
1 $Cu_2(TAMEN)Cl_4$	4,64	52,85	11.92	13.08	10.88	1.76	11
	(5.00)	(53.15)	(12.40)	(12.55)	(11.25)		
2 $Co_2(TAMEN)Cl_4$	5.21	53.08	12.72	12.41	10.21	4.41	18
	(5.04)	(53.59)	(12.50)	(12.65)	(10.52)		
3 $Ni_2(TAMEN)Cl_4$	5.82	52.95	12.15	12.83	10.62	2.98	14
	(5.04)	(53.61)	(12.50)	(12.66)	(10.48)		



Scheme 2 Proposed structure of the complex.

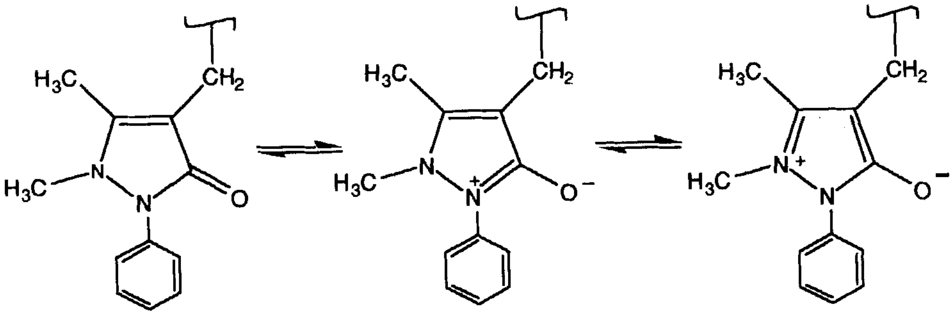
coupling, leading to splitting of the $^4T_1$ (P) term. The spectra of (3) clearly denote a four-coordinated nickel atom.

Infrared spectra of the compounds are somewhat complex. However, some important differences exist between the spectra of the complexes and that of the free ligand. These differences and their assignments are presented in Table 3. In order to explain changes in the spectra, the mesomeric resonance structure of the pyrazolonic fragment must be taken into account (scheme 3), which shows the ability of the carbonyl oxygen atom to coordinate to the metal centre.

The disappearance of the strong C = O stretching vibration band of the free ligand at 1656 cm^{-1} and appearance of bands in the 1156–1166 cm^{-1} region in the spectra

Table 2 Absorption maxima (λ_{mx}) and molar absorptions ε_{max} of the electron transition spectra.

Compound	Nujol	DMF		DMSO	
	λ_{max}/nm	λ_{max}/nm	ε_{max}/l mol^{-1} cm^{-1}	λ_{max}/nm	ε_{max}/l $mol^{-1}cm^{-1}$
1 $Cu_2(TAMEN)Cl_4$	658				
		740	101	761	91
	445	430	820	440	926
2 $Co_2(TAMEN)Cl_4$	695	680	625	677	540
	667 sh				
	629	605	280	605	329
		530	52	526	43
3 $Ni_2(TAMEN)Cl_4$	890	890	10	895	7,0
	626			628	7,0
		372	1095	372	1124



I II III

Scheme 3 Resonance structure of the pyrazolonic ring.

of the complexes denote coordination by carbonylic oxygen. The C = O stretching vibration is shifted in all three complexes to lower frequencies reflecting a weakening of the C = O bond due to coordination. No IR absorption is found for an undisturbed C = O group so that all oxygen atoms seem to coodinate to metal ions. The coordination seems to be strongest for the Ni species. At the same time, the spectra in the 1150–1610 cm^{-1} region become more complicated. In this region two new bands are identified. According to literature[11,12] these bands are assigned to a combination of ν_{C-C} and ν_{C-N} of the resonance structures II and III of the pyrazolonium ion depicted in Scheme 3. This is further evidence that the coordinating structures II and III are present in the complex.

In the far IR spectra, characteristic metal-nitrogen, metal-halide and metal-oxygen vibrations suggest that each metal ion coordinates to two carbonyl groups, one nitrogen group and one chloride ion to form a more or less distorted tetrahedron. The disruption seems to be strongest in the copper complex and this can be explained by the Jahn-Teller effect. In the far IR spectra, Table 3, the vibrational modes of metal-oxygen at 608–610 cm^{-1} and metal-nitrogen at about 380 cm^{-1} are recognized.[13] Bands assigned to the ν_{M-Cl} bonds appear in the region

Table 3 IR and far IR absorption maxima in cm^{-1} and assignments for the free ligand and the complexes.

TAMEN	$Cu_2(TAMEN)Cl_4$	$Co_2(TAMEN)Cl_4$	$Ni_2(TAMEN)Cl_4$	Assignment
		IR-Spectra		
1656 vs				$\nu_{C=O}$
	1632 s	1632 s	1622	$\nu_{C=O}$
1590 m	1590 m	1598 m	1595 m sh	phenyl ring
	1602 m	1608 m	1610 m	pyrazolonium ion
	1574 m	1574 sh m	1580 m	$\nu_{C=C}/\nu_{C=N}$
	1188m	1178 w	1174m	ν_{C-O}
	1156w	1158 w	1150 w	ν_{CO-M}
		Far-IR-Spectra		
	609	608	610	ν_{M-O}
	383	379	383	ν_{M-N}
	222	218	217	ν_{M-Cl}

vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

217–222 cm^{-1}. The positions of these bands denote terminal M-Cl bonds and confirm four-coordinated metal ions, in accordance with electronic spectra.

Elemental analyses and visible absorption spectra suggest the ability of TAMEN to act as a double-terdentate ligand to form tetrahedrally coordinated dinuclear complexes. Conductivities show that at least once chloride ion per metal centre is able to dissociate in DMSO solution. The far IR spectra clearly denote the presence of metal-nitrogen, metal-oxygen and metal-chloride bonds. The structure of such tetrahedrally coordinated metal ions with the amine nitrogen and the two carbonyl oxygens of each arm of TAMEN causes no strain. Magnetic moments show that the complexes are spin-free and TAMEN gives rise to a weak ligand field.

Acknowledgements

Thanks are due to the "Fonds zur Förderung der Wissenschaftlichen Forschung in Österreich" (Project 8795) for financial support.

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