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METAL(II) COMPLEXES OF TRIDENTATE AND BRIDGING BIS(TRIDENTATE) NEUTRAL THIOSEMICARBAZONES OBTAINED FROM 2-ACETYLPIRIDINE AND THE RELATED 2,2'-PYRIDIL

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The new ligands 2-acetylpyridine-2-methyl-3-thiosemicarbazone (apmt) and di-2-pyridylglyoxal-bis(2-methyl-3-thiosemicarbazone) (pgmt) have been used to prepare metal(II) complexes $[M(\text{apmt})\text{Cl}_2]$ ($M=\text{Mn, Fe, Co}$), $[M(\text{apmt})\text{Cl}]\text{Cl}$ ($M=\text{Ni, Cu}$), $[M_2(\text{pgmt})\text{Cl}_4]$ ($M=\text{Mn, Co}$), $[M_2(\text{pgmt})\text{Cl}_2]\text{Cl}_2$ ($M=\text{Ni, Cu}$) and the polymeric $[\text{Fe}(\text{pgmt})]\text{Cl}_2 \cdot \text{H}_2\text{O}$. The tentative structures of these complexes involve four-, five- and six-coordinate environments for the cations, a tridentate chelation for the apmt ligand and bridging bis(tridentate) behaviour for the pgmt ligand. The novel substances were characterized by IR, ^1H NMR, electronic spectroscopy, conductivity and magnetic moment measurements.

KEYWORDS: synthesis, thiosemicarbazones, complexes, transition metals

INTRODUCTION

Transition metal complexes of heterocyclic thiosemicarbazones have received attention due to their biological significance.¹ Complexes with 2-acetylpyridine thiosemicarbazone (apt) have been previously described. They involve seven-coordinate iron(III)² and four-coordinate copper(II)³ species. In the iron(III) complexes, apt behaves as an anionic ligand (by loss of the ^2N proton), which coordinates *via* the pyridyl nitrogen, the azomethine nitrogen and the sulfur atom as a tridentate ligand. However, the neutral and the anionic form of this NNS-donor ligand are observed with copper(II) complexes. The present work was undertaken to study the coordination properties of ligands related to apt, where the acidic ^2N proton is replaced by a methyl group. In this context, the ligand 2-acetylpyridine-2-methyl-3-thiosemicarbazone (apmt) and the potentially bis(tridentate) ligand di-2-pyridylglyoxal-bis(2-methyl-3-thiosemicarbazone) (pgmt) (Fig. 1) were used to form Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes.

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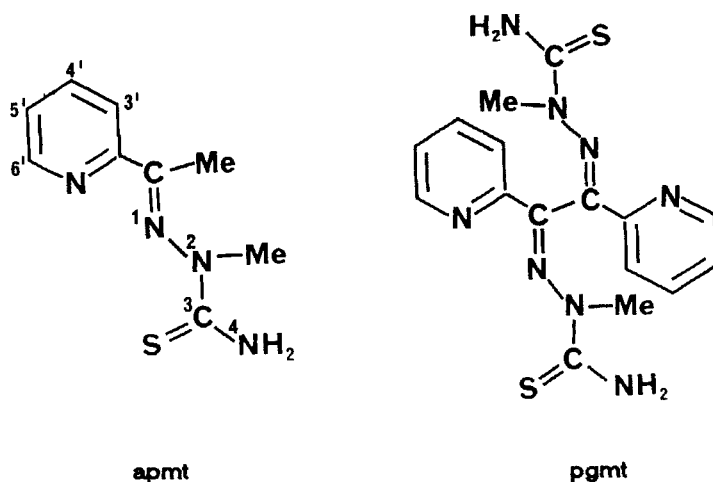


Figure 1 Schematic representation of the ligands apmt and pgmt.

EXPERIMENTAL

All the solvents used in preparing the complexes were reagent grade and were used without further purification. Hydrated chlorides were of analytical grade. 2-methyl-3-thiosemicarbazide, 2-acetylpyridine and 2,2'-pyridil were purchased from Aldrich Chemical Co. IR spectra were recorded on a Bruker Model IFS-66V FTIR instrument. The electronic spectra were obtained on a Spectronic 3000 diode array or a Carl-Zeiss DMR 22 spectrophotometer. ^1H NMR spectra were performed on a Bruker AC-250 P instrument. Magnetic susceptibilities at room temperature were measured by the Faraday method using a Cahn 7600-RTL balance. Conductivities were measured at room temperature in dimethyl formamide (DMF) with a direct lecture L. Pusi instrument.

Reactivity of Superoxide Ion with $[\text{Cu}_2(\text{pgmt})\text{Cl}_2]\text{Cl}_2$

The capacity of the water soluble and stable complex $[\text{Cu}_2(\text{pgmt})\text{Cl}_2]\text{Cl}_2$ to react with O_2^- was determined by using the xanthine-xanthine oxidase method to generate superoxide. The standard ferricytochrome c system was used to scavenge superoxide.⁴

Synthesis of apmt

To a refluxing mixture of 2-methyl-3-thiosemicarbazide (1.52 g, 0.014 mol) and 2-acetylpyridine (1.79 g, 0.014 mol) in MeOH (25 cm³), glacial acetic acid (2 cm³) was added. The solution was refluxed for 30 min and evaporated to dryness. The residue was dissolved in hot benzene (80 cm³), filtered and, upon standing at 10°C for 4 h yellow crystals were formed. The product was isolated by filtration and washed with petroleum ether (20 cm³, 40–60°C fraction). Yield 2.1 g.

Synthesis of pgmt·2HCl

A mixture of 2-methyl-3-thiosemicarbazide (0.210 g, 2 mmol) and 2,2'-pyridil (0.212 g, 1 mmol) in ethanol (10 cm³) was refluxed for 1 min, 1 cm³ of fuming hydrochloric acid (75%) was added and reflux continued for 15 min. The yellow needle like crystals of pgmt·2HCl were washed with ethanol (3 × 3 cm³). Yield 0.230 g. The free base can be precipitated from an aqueous solution (10 cm³) of pgmt·2HCl by addition of concentrated ammonium acetate (5 cm³).

Synthesis of [M(apmt)Cl₂](M=Mn, Co) and [M(apmt)Cl]Cl (M=Ni, Cu)

These complexes were prepared from the reaction of equimolar quantities of the respective hydrated metal chlorides and apmt in refluxing methanol. The following procedure is typical. [Mn(apmt)Cl₂]:MnCl₂·4H₂O (0.150 g, 0.758 mmol) in MeOH (5 cm³) was mixed with apmt (0.158 g, 0.758 mmol) dissolved in MeOH (5 cm³). The resulting mixture was refluxed for 15 min. The yellow crystals were filtered off and washed with MeOH (2 × 3 cm³). Yield 0.195 g.

Synthesis of [Fe(apmt)Cl₂]

Solvent was a mixture of MeOH-dimethoxypropane (2:1 v/v). A solution (15 cm³) of FeCl₂·4H₂O (0.270 g, 1.358 mmol) and ascorbic acid (0.030 g) was rapidly added to a solution (15 cm³) of apmt (0.283 g, 1.358 mmol). The dark blue solution was stirred for 20 min. The crystals that separated were filtered off and washed with MeOH-dimethoxypropane (2:1 v/v; 3 × 5 cm³). Yield 0.415 g.

Synthesis of [M₂(pgmt)Cl₄](M=Mn, Co) and [M₂(pgmt)Cl₂]Cl₂ (M=Ni, Cu)

The general preparative procedure involves the reaction of an excess of the appropriate metal chloride with the free base pgmt in hot methanol. An example of this reaction is the following: [Mn₂(pgmt)Cl₄] To a warm methanol solution (5 cm³) of MnCl₂·4H₂O (0.430 g, 2.173 mmol) was added a hot methanol solution (5 cm³) of pgmt (0.140 g, 0.362 mmol). This mixture was boiled for 10 min, cooled and filtered. The yellow, microcrystalline solid was washed with MeOH (2 × 3 cm³). Yield 0.220 g.

Synthesis of [Fe(pgmt)]Cl₂·H₂O

To a methanol solution (20 cm³) of free base pgmt (0.085 g, 0.220 mmol) and ascorbic acid (0.030 g), solid FeCl₂·4H₂O (0.247 g, 1.242 mmol) was added. The dark blue solution was stirred for 10 min, filtered and vacuum evaporated to reduce the volume to ca. 5 cm³. The formed dark blue crystals were washed with methanol-dimethoxypropane (1:1 v/v, 10 cm³). Yield 0.105 g.

The elemental analyses (Dpto. de Química Orgánica, Fac. Cs. Químicas y Farmacéuticas, Universidad de Chile) of all the new compounds are presented in Table 1.

Table 1 Colours, analytical data and molar conductivity of apmt and pgmt ligands and their complexes.

Compound	Colour	Analysis (%)			Λ_M^b omh ⁻¹ cm ² mol ⁻¹
		C	H	N	
apmt	yellow	52.2(51.9)	6.0(5.8)	26.3(26.9)	—
[Mn(apmt)Cl ₂]	yellow	32.7(32.4)	3.4(3.6)	16.9(16.8)	32
[Fe(apmt)Cl ₂]	dark blue	32.5(32.3)	3.4(3.6)	16.5(16.7)	32
[Co(apmt)Cl ₂]	dark brown	32.2(32.0)	3.7(3.6)	16.9(16.6)	13
[Ni(apmt)Cl]Cl	brown	31.9(32.0)	3.8(3.6)	16.4(16.6)	65
[Cu(apmt)Cl]Cl	dark green	31.2(31.5)	3.7(3.5)	16.5(16.4)	73
pgmt·2HCl	yellow	41.2(41.8)	4.8(4.4)	24.3(24.4)	—
[Mn ₂ (pgmt)Cl ₄]	yellow	30.3(30.1)	3.1(2.8)	17.4(17.6)	— ^c
[Fe(pgmt)]Cl ₂ ·H ₂ O	dark blue	36.0(36.2)	3.6(3.8)	21.3(21.1)	— ^c
[Co ₂ (pgmt)Cl ₄]	dark brown	30.2(29.7)	3.0(2.8)	17.1(17.3)	— ^c
[Ni ₂ (pgmt)Cl ₂]Cl ₂	green	30.0(29.8)	2.9(2.8)	17.6(17.4)	— ^c
[Cu ₂ (pgmt)Cl ₂]Cl ₂	dark green	29.5(29.3)	3.0(2.8)	17.3(17.1)	— ^c

^a Required values are given in parentheses. ^b ca.10⁻³ M in DMF. ^c insoluble.

RESULTS AND DISCUSSION

Characterization of the Ligands

The analytical data for the new ligands apmt and pgmt (Fig. 1) are listed in Table 1. The solid state IR spectra of both ligands are characterized by three strong bands at 3421–3134 cm⁻¹ due to the ⁴N-H stretching vibrations,² a very strong absorption at 1596(apmt) and 1584(pgmt) cm⁻¹ assigned to $\nu(C=N)$,² a very strong band at 866(apmt) and a medium to strong band at 909(pgmt) cm⁻¹ attributed to $\nu(C=S)$,^{3,5} and a medium band at 405 cm⁻¹ assignable to a pyridine ring deformation.⁶

The apmt ligand has the expected ¹H NMR spectrum in CDCl₃.⁷ In particular, the ⁴NH₂ protons are observed as a broad band at 6.40 ppm (2H). The signals for the acetyl methyl and ²NCH₃ groups appear at 2.02 ppm (3H) and 3.68 ppm (3H), respectively. The doublets at 8.67 (1H) and 8.12 ppm (1H) are due to the pyridyl ring protons on the C-6' and C-3' carbon atoms, respectively. The triplet at 7.78 ppm (1H) is assigned to the C-4' proton, while the quartet at 7.41 ppm (1H) can be assigned to the proton on C-5'.

The ¹H NMR spectrum of the free base pgmt, in CDCl₃, exhibits two singlets at 3.90 and 3.86 ppm (integration ratio approximately 2.5:1) assigned to methyl protons. A complex system of three groups of multiplets and a broad singlet between 8.80 and 6.60 ppm can be assigned to the pyridyl and ⁴NH₂ protons. The existence of different intensities for the methyl protons and the multiplicity of signals for the pyridyl protons, may indicate the existence of an unequal population of two isomers in solution.⁷

Characterization of the Complexes

Colours, analytical data and conductivity values for the complexes are given in Table 1. The crystalline complexes are stable under atmospheric conditions and

insoluble in acetone, benzene and dichloromethane. The apmt complexes are slightly soluble in DMF, while those of pgmt are insoluble. All the compounds are soluble in water with clear changes in their electronic spectra with time, except the Cu(II) complexes which are quite stable (pgmt > apmt). The molar conductivities, in DMF (Table 1), of the aptm complexes with Mn(II), Fe(II) and Co(II) were found to be non-electrolytes, whereas the data for the Ni(II) and Cu(II) complexes are consistent with 1:1 behaviour.⁸ The conductance of the complexes with pgmt could not be determined due to insolubility.

Infrared Spectra

The main IR bands of the ligands apmt and pgmt and their metal complexes are listed in Table 2. The strong $\nu(\text{C}=\text{N})$ bands at 1596 (apmt) and 1584 (pgmt) cm^{-1} of the free ligands are shifted to 1632–1623 cm^{-1} and 1641–1631 cm^{-1} in the complexes respectively, indicating coordination of the azomethine nitrogen.² The $\nu(\text{C}=\text{S})$ vibrations in the free ligands (Table 2) exhibit a decrease of their intensity in all the complexes. This observation, the appearance of new bands in the apmt complexes at 824–812 cm^{-1} and the increase in intensity of those of the pgmt complexes at 881–868 cm^{-1} , suggest coordination of the thiocarbonyl sulfur to the metal ions.⁹ Coordination of a pyridyl nitrogen is usually indicated by an increase in energy of the ring deformation mode⁶ at ca. 405 cm^{-1} ; in all the complexes this mode is shifted to 422–410 cm^{-1} .

In the far infrared, several new bands are observed in the spectra of the complexes, typical of the M-S, M-Cl and M-Npy vibrations^{5a} (Table 2). Furthermore, the number of $\nu(\text{M}-\text{Cl})$ bands at 303–238 cm^{-1} seems to be indicative of the number of chloro-ligands coordinated per metal ion. The Ni(II) and Cu(II) complexes exhibit only one strong band; in the Mn(II) and Co(II) complexes there are two bands. Two bands appear for the Fe(II)-apmt complex and only in the Fe(II)-pgmt complex are they absent.

Solid State Electronic Spectra

Magnetic moments at room temperature and the solid state electronic spectra of the

Table 2 Infrared spectra^a of the metal(II) complexes with apmt and pgmt.

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S})$	Pyridine ring deformation	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{Cl})$	$\nu(\text{M}-\text{Npy})$
apmt	1596br,vs	866 vs	405	—	—	—
[Mn(apmt)Cl ₂]	1623vs	812m	413m	300(sh)	280(sh),270(sh)	258s
[Fe(apmt)Cl ₂]	1623vs	812m	416m	304w	276m,238m	257s
[Co(apmt)Cl ₂]	1623vs	813m	420m	305w	287vs,243ms	257ms
[Ni(apmt)Cl]Cl	1625vs	822m	422m	318m	277s	260s
[Cu(apmt)Cl]Cl	1632vs	824m	419m	315(sh)	303s	260mw
pgmt	1584vs	909ms	405m	—	—	—
[Mn ₂ (pgmt)Cl ₄]	1631vs	875m	410m	308w	283m, 275m	256ms
[Fe(pgmt)]Cl ₂ ·H ₂ O	1641br,vs ^b	880m	412br,m	325w, 311w	—	242w
[Co ₂ (pgmt)Cl ₄]	1635vs	868m	413m	319br,mw	281s,264s	245s
[Ni ₂ (pgmt)Cl ₂]Cl ₂	1633vs	881m	412m	320br,mw	281s	252m
[Cu ₂ (pgmt)Cl ₂]Cl ₂	1639vs	878m	415m	321mw	300s	263mw

^a cm^{-1} ; KBr and polyethylene pellets. ^b Include some contribution of the H₂O bending.

complexes are presented in Table 3. The manganese(II) complexes have five unpaired electrons on each metal center and the electronic spectra are not informative about the environment of the metal ions. Hence, a five-coordinate geometry for the $[\text{Mn}(\text{apmt})\text{Cl}_2]$ complex is suggested on the basis of the IR spectra and conductivity results (*vide supra*). The pgmt complex is formulated as the bimetallic complex $[\text{Mn}_2(\text{pgmt})\text{Cl}_4]$ due to the similarity of its IR and electronic spectra with those of the $[\text{Mn}(\text{apmt})\text{Cl}_2]$. Consequently, apmt acts as a tridentate ligand and pgmt as a bridging bis(tridentate) ligand.

The *d-d* bands in the electronic spectra of the mononuclear $[\text{Fe}(\text{apmt})\text{Cl}_2]$ ($10,000\text{ cm}^{-1}$) and $[\text{Co}(\text{apmt})\text{Cl}_2]$ ($6900, 9500, 15,400, \text{ and } 19,600\text{ cm}^{-1}$) are comparable to those reported for five-coordinate high spin complexes, for which distorted square pyramidal structures have been proposed.¹⁰ The spectrum of $[\text{Fe}(\text{apmt})\text{Cl}_2]$ presents, in addition to the *d-d* band at $10,000\text{ cm}^{-1}$, a broad and strong band at $17,300\text{ cm}^{-1}$ which we attribute to a charge-transfer absorption. The similarity of spectra for the $[\text{Co}(\text{apmt})\text{Cl}_2]$ and $[\text{Co}_2(\text{pgmt})\text{Cl}_4]$ complexes suggest near identical environments for the cobalt atom in these complexes, implying that pgmt serves as a bridge between the metal centers.

The 1:1 iron(II) complex with pgmt, isolated in this study, is diamagnetic and the electronic spectrum shows the typical spin allowed absorptions ${}^1\text{T}_{1g} \leftarrow {}^1\text{A}_{1g}$ and ${}^1\text{T}_{2g} \leftarrow {}^1\text{A}_{1g}$ for an octahedral configuration at $12,500$ and $15,000\text{ cm}^{-1}$, respectively.¹¹ The strong bands at $17,240$ and $18,860\text{ cm}^{-1}$ are assigned to charge-transfer absorptions.¹² Low-spin, octahedral Fe(II) complexes have been observed with the related ligand pyridine-2-carbaldehyde thiosemicarbazone (pct).^{12,13} In this case, the Fe(II) is surrounded by two pct ligands, each coordinating as a planar tridentate (NNS) ligand in a *mer*-isomer arrangement.¹⁴ Therefore, the formulation of the Fe(II)-pgmt complex as the hexa-coordinated polymeric $[\text{Fe}(\text{pgmt})\text{Cl}_2 \cdot \text{H}_2\text{O}]$ with bridging pgmt and uncoordinated chlorides, is more consistent with the observed IR and electronic spectra.

The electronic spectrum of the paramagnetic $[\text{Ni}(\text{apmt})\text{Cl}]\text{Cl}$ complex with strong and broad visible band ${}^3\text{T}_1(\text{P}) \leftarrow {}^3\text{T}_1(\text{F})$ at $12,000\text{ cm}^{-1}$ and the weak band ${}^3\text{A}_2 \leftarrow {}^3\text{T}_1(\text{F})$ at 7000 cm^{-1} indicates a pseudotetrahedral stereochemistry for the nickel (II) ion.¹⁵ Likewise, the bands for the Ni(II)-pgmt complex (Table 3) are also compatible with a pseudotetrahedral arrangement around Ni(II) and could be formulated as the binuclear pgmt-bridged $[\text{Ni}_2(\text{pgmt})\text{Cl}_2]\text{Cl}_2$ complex.

Table 3 Solid state electronic spectra and magnetic moments of the metal(II) complexes with apmt and pgmt.

Complex	Electronic spectra ^a (cm^{-1})	μ_{eff} (B.M.)
$[\text{Mn}(\text{apmt})\text{Cl}_2]$	—	6.1
$[\text{Fe}(\text{apmt})\text{Cl}_2]$	10,000w, 17,300vs,br	5.0
$[\text{Co}(\text{apmt})\text{Cl}_2]$	6900w, 9500w, 15,400s, 19,600s	4.3
$[\text{Ni}(\text{apmt})\text{Cl}]\text{Cl}$	7000w, 12,000s, vbr	3.3
$[\text{Cu}(\text{apmt})\text{Cl}]\text{Cl}$	13,300br	1.8
$[\text{Mn}_2(\text{pgmt})\text{Cl}_4]$	—	5.8 ^b
$[\text{Fe}(\text{pgmt})\text{Cl}_2 \cdot \text{H}_2\text{O}]$	12,500w, 15,000sh, 17,240vs, 18,860vs	dia.
$[\text{Co}_2(\text{pgmt})\text{Cl}_4]$	7400w, br, 15,900s, 20,000s	4.3 ^b
$[\text{Ni}_2(\text{pgmt})\text{Cl}_2]\text{Cl}_2$	7100w, 12,050s,br, 15,150sh	3.3 ^b
$[\text{Cu}_2(\text{pgmt})\text{Cl}_2]\text{Cl}_2$	14,300br	1.8 ^b

^aNujol mull. ^bper metal ion.

The similarity of the IR and electronic spectra for the copper(II) complexes prepared with apmt and pgmt, indicate their formulation as $[\text{Cu}(\text{apmt})\text{Cl}]\text{Cl}$ and $[\text{Cu}_2(\text{pgmt})\text{Cl}_2]\text{Cl}_2$ species. The magnetic moments of these compounds are normal for a copper(II) ion. Their electronic spectra, in the visible region, are similar to those reported either for square planar¹⁶ or distorted tetrahedral species.¹⁷ Nishida *et al.*¹⁷ have suggested that distorted tetrahedral complexes of copper(II) react with the superoxide anion (superoxide dismutase activity) whereas such activity is not detected with square planar species. Our experimental results show that the stable binuclear copper(II) complex $[\text{Cu}_2(\text{pgmt})\text{Cl}_2]\text{Cl}_2$ interacts with the O_2^- ion.

Electronic Spectra in DMF Solution

The electronic spectra of the apmt complexes, which are slightly soluble in DMF, are presented in Figure. 2. A similar pattern is observed in comparison with measurements in the solid state (Table 3), suggesting the same environment for the metal centers in both media.

Biological Activity

Since the copper(II) complex $[\text{Cu}_2(\text{pgmt})\text{Cl}_2]\text{Cl}_2$ is the most stable in water, among the series of new complexes prepared in this work, it was selected as a probe for biological tests. This binuclear compound exhibits a marked biological activity against eukaryotic organisms, such as *Daphnia Pulex* ($EC_{50} = 30 \mu\text{M}$) and human lymphocyte culture (100 μg have 84% antimetabolic activity), but it has no effect on a prokaryotic *E. Coli* culture. On the other hand, the superoxide dismutase-like

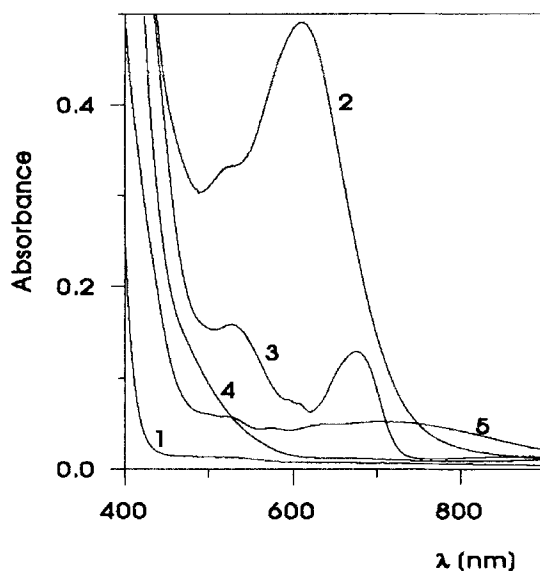


Figure 2 Electronic spectra in DMF (10^{-3} M) of: (1) $[\text{Mn}(\text{apmt})\text{Cl}_2]$, (2) $[\text{Fe}(\text{apmt})\text{Cl}_2]$, (3) $[\text{Co}(\text{apmt})\text{Cl}_2]$, (4) $[\text{Ni}(\text{apmt})\text{Cl}]\text{Cl}$ and (5) $[\text{Cu}(\text{apmt})\text{Cl}]\text{Cl}$. The spectra were obtained with a Spectronic 3000 diode-array spectrophotometer.

activity of the $[\text{Cu}_2(\text{pgmt})\text{Cl}_2]\text{Cl}_2$ complex was measured. The concentration of the scavenger complex required to halve the initial rate of reduction of ferricytochrome c was 4.6×10^{-4} M. This value compares in magnitude with those of other Cu(II) complexes with ligands such as o-phen (2×10^{-4} M) and salicylate (4×10^{-4} M).⁴

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