Thermal properties of some transition metal nitroso and thiobarbiturate complexes: conductivity, magnetism and thermogravimetry

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Abstract

Some nitroso and thiobarbiturate complexes were studied under different temperatures using conductivity, magnetic susceptibility and thermogravimetric techniques. The complexes show semi-conductor behaviour. The energies of activation were calculated and discussed. The dielectric constants and the dielectric loss values were evaluated. The superexchange mechanism of the complexes was explained.

INTRODUCTION

The nitroso compounds are biologically active with anti-bacterial and anti-viral properties [1]. The barbiturate compounds affect motor functions and the nervous system [2]. The coordination chemistry of the nitroso [3–15] (**I**) and the barbiturate [16–25] (**II**) compounds has been thoroughly investigated in our laboratory using different physicochemical methods of analysis. The present study investigates some thermal properties from the conductivity and magnetic susceptibility measurements of some nitroso and barbiturate complexes.

X = –COOH & –CH$_3$

(I)

(II)

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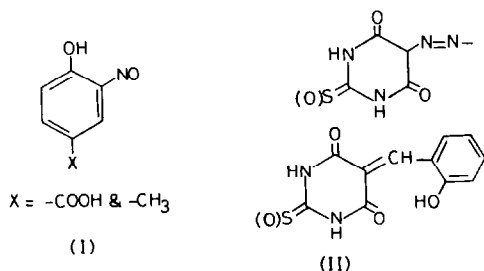
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Some physical constants, namely energy of activation (ΔE), dielectric constant $(\bar{e})$, dielectric loss $(\tan \delta)$ and Curie–Weiss constants (θ), are evaluated and discussed.

EXPERIMENTAL

The nitroso complexes were prepared by the usual method of nitrosating the corresponding phenol (p-hydroxybenzoic acid and p-cresol) with $NaNO_2$ and HCl in the presence of the corresponding transition metal salt (Co(II), Ni(II) and Cu(II)) [26]. The analytical data (Table 1) confirmed the formation of 1:2 and 1:3 complexes.

The thiobarbiturate and its condensed product with salicylaldehyde, together with $PdCl_2$ and H_2PtCl_6 in ammoniacal alcoholic solution gave the corresponding complexes. The analytical data (Table 2) indicate their

TABLE 1

Analytical data for nitroso complexes

Complex	Stoichiometry	Calculated (Found) (%)	
		N	M
Cobalt(4-carboxy-2-nitrosophenol)	1:3	10.6	7.5
		(10.5)	(7.5)
Nickel(4-carboxy-2-nitrosophenol)	1:3	10.5	7.5
		(10.6)	(7.5)
Copper(4-carboxy-2-nitrosophenol)	1:2	16.1	7.1
		(16.2)	(7.5)
Cobalt(4-methyl-2-nitrosophenol)	1:3	12.6	9.0
		(12.6)	(8.7)
Nickel(4-methyl-2-nitrosophenol)	1:2.3 H_2O	15.3	7.3
		(15.2)	(7.2)
Copper(4-methyl-2-nitrosophenol)	1:3.4 H_2O	11.7	7.7
		(11.5)	(7.7)

TABLE 2

Analytical data for palladium and platinum thiobarbituric acid complexes

Complex	Stoichiometry	Calculated (Found) (%)			
		C	H	N	M
Palladium thiobarbituric acid	1:4.4 H_2O	25.5	2.7	14.9	14.1
		(25.8)	(2.9)	(15.2)	(13.6)
Palladium salicylidene thiobarbituric acid	1:1.6 H_2O	28.6	4.1	6.1	23.1
		(28.8)	(4.7)	(6.1)	(23.4)
Platinum thiobarbituric acid	1:2 H_2O	19.9	1.4	11.6	
		(20.7)	(1.5)	(12.1)	

existence in mole ratios of $1:1$, $1:2$ and $1:4$. The azo barbiturate compounds and their complexes were prepared.

The conducting properties were measured by means of an electrometer, type VA-J-52, and a d.c. source. Compressed pellets of 1 cm^2 area and 0.2–0.5 cm thickness were moulded at room temperature at a pressure ranging from 150 to 200 kg cm^{-2}. The system was connected to a vacuum line and outgassed for 24 h to remove moisture.

Thermogravimetry measurements (TG) were made with a Du Pont 950 thermobalance. 10 mg of the sample was heated at $10\,°C$ min^{-1} in a dynamic nitrogen atmosphere (70 ml min^{-1}). The sample holder was boat-shaped 10 mm $\times$ 5 mm and 2.5 mm deep, and the temperature-measuring thermocouple was placed at a distance of 1 mm from the sample holder. The initial rate of decomposition was measured using TG at different intervals. The DTA curves were obtained using a Du Pont 900 instrument with small glass beads as reference. The sample was heated at 10 K min^{-1} from ambient temperature to $500\,°C$ in a nitrogen flow (80 ml min^{-1}).

The magnetic susceptibility measurements were carried out at different temperatures using the Gouy method. Diamagnetic corrections were made using Pascal's constants. Hg[Co(SCN)$_4$] was used as a calibrant.

RESULTS AND DISCUSSION

Electrical conductivity

Figures 1 and 2 show the variation of the logarithmic electrical conductivity values of two selected compounds (one being an electron donor –CH$_3$, and the other an electron-attractor –COOH) as a function of the reciprocal absolute temperature. Straight lines were obtained indicating semiconducting behaviour rather than metallic conductors [19], or that promotion of electrons from ground to excited states may be necessary before conduction occurs [19]. The first step in the conduction process is the excitation of an electron from the uppermost filled orbitals to the lowest π molecular orbital. It is then assumed that the electron tunnels to the equivalent empty level of the neighbouring molecule in the direction of the anode, whereas the positive hole moves to a molecule in the opposite direction towards the cathode. The measurements fit with the relation

$$\sigma = \sigma_0 \exp(-\Delta E/2KT)$$

where σ is the specific conductivity, ΔE the activation energy, σ_0 a constant for the conductivity independant of temperature and K the Boltzman constant. The electrical conductivity data are compiled in Table 3.
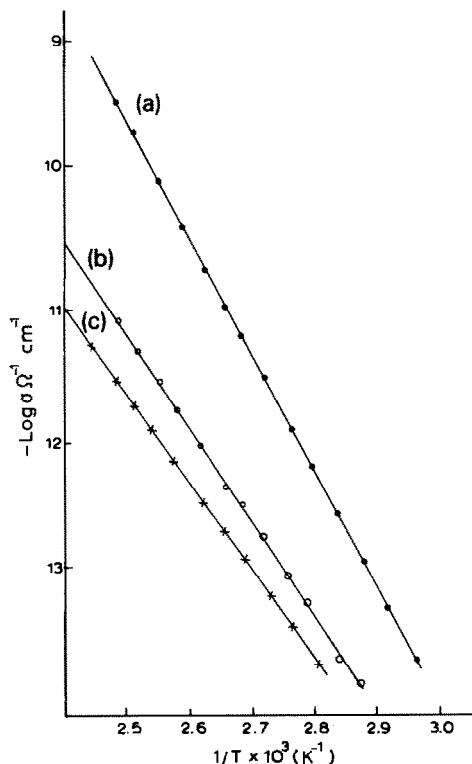
Fig. 1. $-\text{Log }\sigma$ versus $1/T$ relationships for 4-methyl-2-nitrosophenol complexes: (a) Cu; (b) Ni; (c) Co.

Insoluble metal chain complexes with interaction between adjacent atoms in the polymeric structure could supply a convenient route for conduction by charge carrier. During thermal agitation, an additional increase in electrical conductivity occurs, probably leading to a discontinuity in the chemical bonds existing in the samples. The data indicate that the metal ion forms a bridge between the two ligands, thus facilitating the transfer of current carriers during measurements leading to an increase in the electrical conductivity with a decrease in the energy of activation. Consistent with this is the possibility of some degree of delocalization in the excited state, but little or none can be expected in the ground state. The p-methylnitrosophenol complexes possess higher conductivities than those of the p-carboxy. The conductivity of the copper compounds is higher than those of the cobalt and nickel compounds over the temperature range studied. The copper atom contains one more electron than the nickel atom. This electron will occupy the $d_{x^2-y^2}$ orbital and takes part in inter-metallic interactions.

Figure 3 gives the electrical conductivity data of palladium thiobarbituric acid, platinum thiobarbituric acid and palladium thiobarbituric acid salicyli-
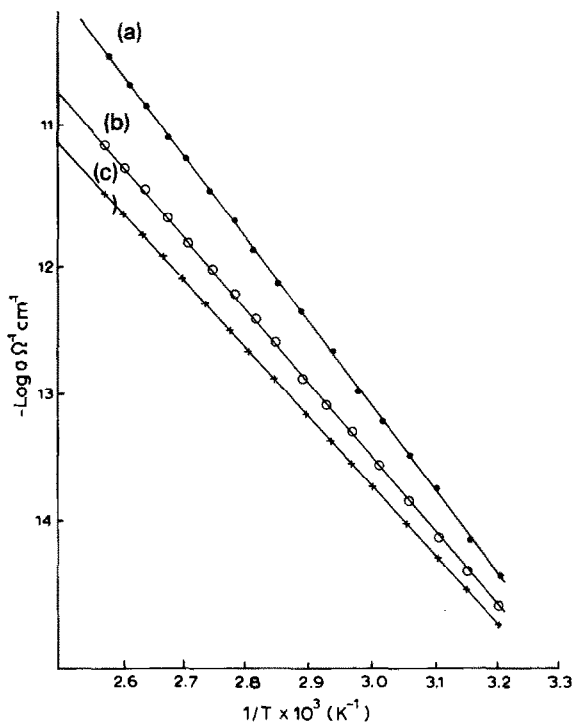
Fig. 2. $-\log \sigma$ versus $1/T$ relationships for 4-carboxy-2-nitrosophenol complexes: (a) Cu; (b) Ni; (c) Co.

TABLE 3

Electrical conductivity results for the complexes

| Complex	ΔE (eV)	$\log \sigma_0$
Cobalt(4-methyl-2-nitrosophenol)	1.31	4.87
Nickel(4-methyl-2-nitrosophenol)	1.40	6.45
Copper(4-methyl-2-nitrosophenol)	1.80	13.45
Cobalt(4-carboxy-2-nitrosophenol)	0.99	1.37
Nickel(4-carboxy-2-nitrosophenol)	1.07	2.84
Copper(4-carboxy-2-nitrosophenol)	1.24	5.85
Palladium thiobarbituric acid	−0.11	−7.44
	0.58	0.55
	1.06	11.32
Palladium salicylidene thiobarbituric acid	−0.18	−9.17
	0.34	−2.50
	1.01	9.46
Platinum thiobarbituric acid	0.50	1.34
	0.80	6.05
	1.72	20.82
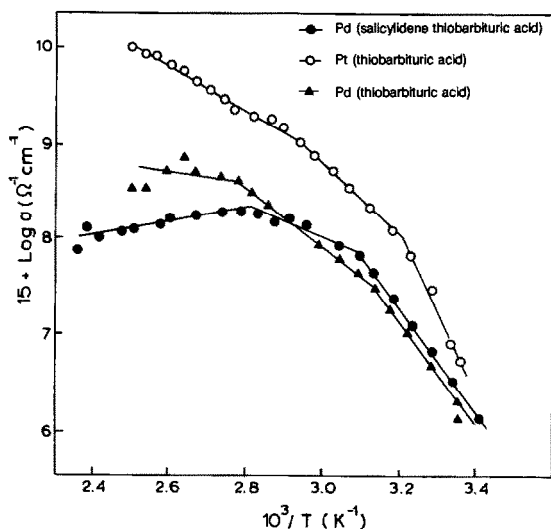
Fig. 3. Electrical conductivity–temperature relationships.

dene complexes. In general all these complexes show three breaks and a discontinuation in the conductivity curves. This can be ascribed to a molecular rearrangement or to crystallographic transitions [19]. As the temperature increases, the conductivity values are increased. There is considerable similarity between palladium thiobarbituric acid and its condensed product but with some varations in the third break of the curve. The conductivity of the former is higher than that of the latter owing to the conjugation. The Pt–SBA complex has a higher conductivity than the Pd–SBA complex, probably due to the difference in the forces of interaction in both complexes. The lower conductivity weakens the conjugation in the chelate rings due to its packing property [19] based on the interaction of the metal orbitals with the organic compound to give new delocalized molecular orbitals. This is affected by the distortion in the conduction pathway caused by the lattice imperfection controlled by the movement of electrons.

For the energy of activation (ΔE), three values are obtained for each one of the three complexes where $\Delta E_1 > \Delta E_2 > \Delta E_3$ and $\Delta E_{Pt-SBA} > \Delta E_{Pd-SBA} > \Delta E_{Pd-SBA-Sal}$. Empirical equations are correlated between ΔE and log σ_0 values for these systems.

Best fit straight lines are obtained, see Fig. 4. Plotting the electric loss (tan δ) versus frequency, Fig. 5 shows that the electric loss is frequency independent in the first region and increases in the second region. The log f–log σ relation (Fig. 5) shows that as the frequency increases, the conductivity values increase. The permittivity $\bar{\varepsilon}$–log f relation, Fig. 5, gives two regions. The dependence of the frequency on the dielectric constant shows a strong dispersion of permittivity in two regions. In the first region
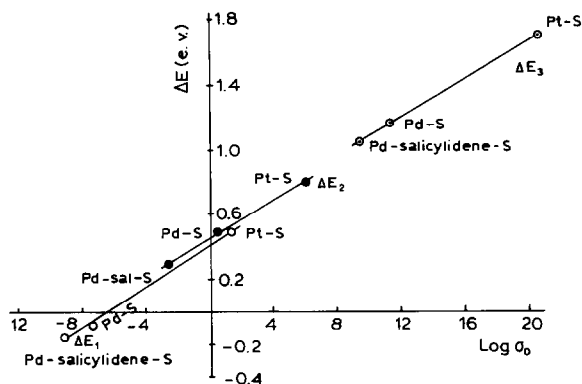
Fig. 4. ΔE versus log σ_0 relationship for palladium and platinum complexes.

$\bar{\varepsilon} \propto \bar{w}^n$ where w is the angular frequency; in the second region, $\bar{\varepsilon} \propto w^n$ which shows abnormal behaviour.

Thermogravimetric studies

The thermogravimetric analyses of six selected azo complexes are given in Fig. 6. The Co–CHO complex with stoichiometry 2:1.4 H_2O and
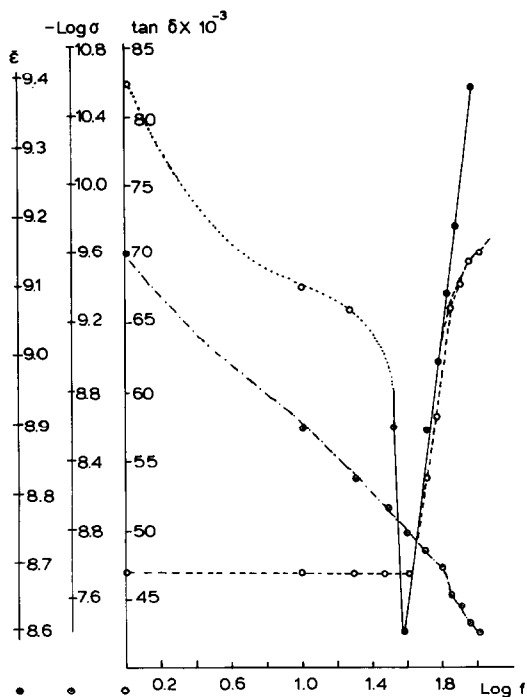

Fig. 5. ○ Electric loss (tan δ) versus frequency (f). ⊙ Logarithmic electrical conductivity (log σ) versus frequency (f). ● Dielectric constant ($\bar{\varepsilon}$) versus frequency (f).
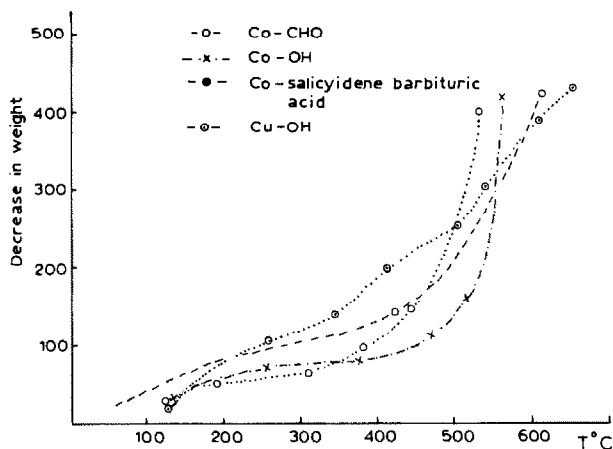
Fig. 6. Thermogravimetric analyses.

molecular formula $Co_2C_{11}H_{14}N_4O_8$ decomposes as follows. The complex changes slightly with temperature up to $300\,°C$, corresponding to the loss of one molecule of water. Then there is a sharp decrease in weight giving different decomposition products. Further decomposition occurs with successive increase in temperature (from 380 to $520\,°C$) with a slight change in weight. In this temperature range, two parts of the decomposition curve are apparent: the first due to elimination of three water molecules, the second due mainly to the formation of different decomposition products, mostly Co, NO and N_2. At high temperature, the complex rapidly decomposites with formation of Co_3O_4 and Co. Therefore, the decomposition fragmentation is in accordance with the proposed structure of the complex [27] shown in Scheme 1.

However, the copper complex derived from the hydroxy ligand with the molecular formula $Cu_2C_{10}H_{16}N_4O_9$ and stoichiometry $2:1.5\ H_2O$ gives different steps for decomposition as the temperature increases. In the temperature range $120–350\,°C$, two molecules of water in the outer sphere of the complex are first envolved. On further increase in temperature, the inner water molecules are lost. According to the loss in weight calculation at different temperatures, the decomposition products are $9CuO + 2.75CO_2 + 9NO_2 + 7H_2O + 6N_2O_3$. This agrees with the proposed structure shown in Scheme 2 [27].
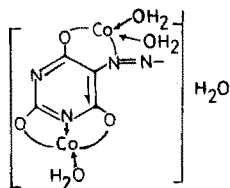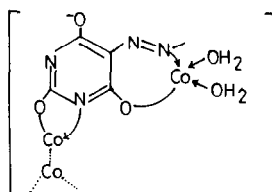

Scheme 1.
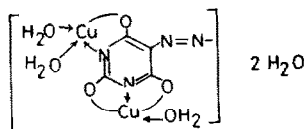
Scheme 2.
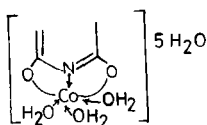
Scheme 3.

Scheme 4.

The data of the cobalt hydroxy complex, with stoichiometry $2:1.6$ H_2O, are very similar to those of the copper hydroxy complex. Two peaks are obtained: the first rounded and the second sharp. The final decomposition product is not pure oxide but contains some unoxidised carbonaceous matter. This slowly oxidises as the temperature increases until pure oxide is obtained. From the loss-in-weight–temperature data, the decomposition products are $3CoO_3 + NO + NO_2 + 10H_2O + 2NH_3 + 4.5CO_2 + 1.5N_2$. Therefore, the structure of this complex is similar to the cobalt complex discussed above [27].

The thermolysis curve of the $Co-NO_2$ complex with stoichiometry $1:1.8$ H_2O and molecular formula $CoC_{10}H_{22}N_5O_{13}$ was investigated. The solvated chelate is stable up to $120\,°C$, where it begins to lose water. A break in the curve at $220\,°C$ corresponds closely to the normal chelate. Then it decomposes slowly on further heating without a clear weight loss. The presence of a number of water molecules gives many different steps. When the number of water molecules is taken to be 8, the results of the elemental analyses agree with the theoretical numbers. According to the stereochemistry of this complex obtained from electronic spectra and magnetic susceptibility measurements, and from the mode of bonding based on the IR spectra, the structure is as shown in Scheme 3.

The proposed structure for the cobalt methyl complex [27] is shown in Scheme 4.

The complex with $3:1.x$ H_2O stoichiometry thermally decomposes in a similar fashion to the previously discussed complexes. However, the cobalt–cobalt interaction needs a higher energy for decomposition, which was not the case for the other complexes due to the presence of the extra transition element.

Magnetic susceptibility measurements

The magnetic moment values for the nitroso complexes are shown in Table 4, while those of the azo complexes are collected in Table 5. Wide changes in these values are obtained for both systems. Low values for the nitroso complexes of the ordered magnetic moment of Cu(II) (less than 0.5 μ_B, instead of 1.00 μ_B expected for $g = 2$) were obtained. This suggests that the copper ions cannot carry a localized magnetic moment. This is a

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TABLE 4

θ and μ values at different temperatures for nitroso complexes (Fig. 7)

Compound	θ	Temperature (K)													
		110	135	155	175	195	215	230	250	270	280	300	325	340	370
1	103		0.058	0.057	0.057	0.059	0.059	0.059	0.058	0.058	0.058	0.059	0.059	0.059	
2	50	0.057	0.057	0.057	0.058	0.058	0.057	0.057	0.058	0.059	0.060	0.059	0.059	0.060	
3	105	0.032		0.038		0.042		0.045		0.048		0.050			
4	210	0.032	0.035	0.038	0.041	0.044	0.046	0.048	0.051	0.052	0.053	0.055	0.054	0.053	
	390														

TABLE 5

θ and μ values at different temperatures for azo complexes (Fig. 8)

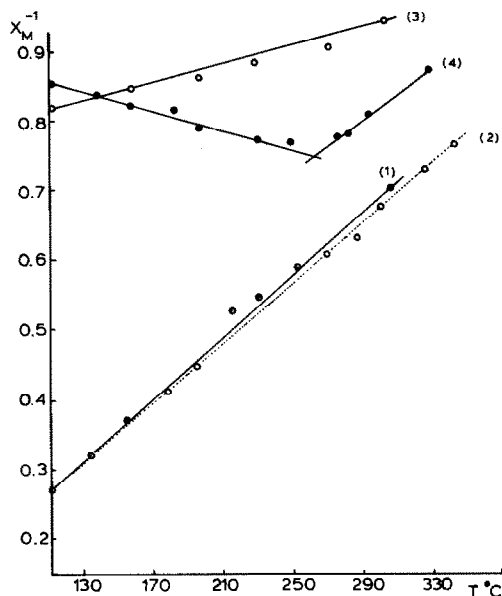| Compound	θ	Temperature (K)																
		200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	360	370
1	271									4.25	2.74	2.27	1.99	1.79	1.65	1.55		
2	200	2.61	5.74	3.96	3.16	2.80	2.47	2.32	2.17	2.05	1.96	1.90	1.74	1.13		1.03	0.96	0.93
3	140			2.48		2.35		2.18			2.17	2.13		2.09		2.04	2.01	
4	222					2.59		1.84		1.54		1.38		1.27		1.20		
5	180		2.80		2.31	2.17		1.94	1.88		1.75	1.71		1.63		1.57	1.53	
6	225					2.79	2.21	1.89	1.68	1.56	1.46	1.38	1.32	1.27	1.22	1.18		

Fig. 7. Magnetic susceptibility data at different temperatures for the nitroso complexes: (1) copper(4-carboxy-2-nitrosophenol)$_2$; (2) copper(4-methyl-2-nitrosophenol)$_3 \cdot 4H_2O$; (3) nickel(4-methyl-2-nitrosophenol)$_2 \cdot 3H_2O$; (4) nickel(4-carboxy-2-nitrosophenol)$_3$.

characteristic feature of the ordering of the 3d-hole of the Cu(II) ions in the e$_g$ and d$_{x^2-y^2}$ orbitals [28]. Very small magnetic moment values for all the nitroso complexes (0.032–0.06 μ_B) were obtained, independent of
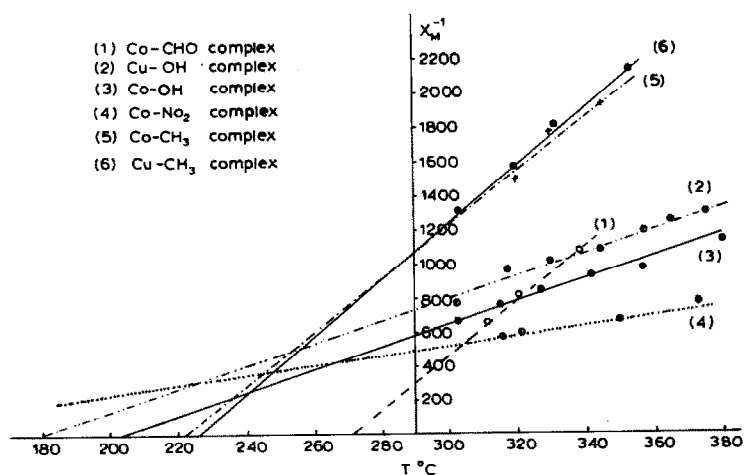

Fig. 8. Magnetic susceptibility data for azo complexes at different temperatures.

temperature. This is accounted for by assuming the existence of polymeric structures in the solid state via Cu–Cu interaction and may be ascribed to a super exchange mechanism. The sub-normal values are indicative of some extended interaction leading to an anti-ferromagnetic exchange property [14,15]. This is confirmed by calculating the θ values that lie in the range 50–390, see Table 4 and Fig. 7. However, for the azo complexes the magnetic moment and the θ values are very high, see Fig. 8 and Table 5, compared to the nitroso system (Table 4). Also, the μ values decrease with increasing temperature. It seems that the geometry of these complexes is probably temperature dependent [19]. Also, at low temperature, the spin orbital contribution is of major importance in controlling the behaviour of these complexes. This leads to an increase in the μ values and the spin moment contribution is clearly identified at higher temperatures.

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