

## **Synthesis and Characterization of Co(II), Ni(II), and Cu(II) Complexes of Salicylal-4-aminoantipyrine and 2-Hydroxy-1-naphthol-4-aminoantipyrine and their Adducts**

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**Summary.** The electrochemical oxidation of anodic Co, Ni and Cu in acetone solutions of 4-aminoantipyrine Schiff base of salicylaldehyde (*SAAP*) and 2-hydroxy-1-naphthaldehyde (*NAAP*) [= R(OH)] gave the title complexes in high yields. When neutral mono- or bidentate donors were present in the solution, the products were the 1 : 1 adducts of mixed complexes. The complexes were characterized by elemental analysis, IR, electronic, and ESR spectra as well as magnetic moment measurements. The thermal (DTA) behaviour and electrical properties of some complexes were investigated in the solid state and correlated with the structure of the complexes.

**Keywords.** Electrochemistry; Transition metals; Schiff base; Complexes.

### **Synthese und Charakterisierung von Co(II), Ni(II) und Cu(II)-Komplexen von Salicylal-4-aminoantipyrinen und 2-Hydroxy-1-naphthol-4-aminoantipyrinen und ihren Addukten**

**Zusammenfassung.** Die elektrochemische Oxidation von Co, Ni und Cu in Lösungen von 4-Aminoantipyrin-Schiff-Basen von Salicylaldehyd (*SAAP*) und 2-Hydroxy-1-naphthaldehyd (*NAAP*) ergab die im Titel genannten Komplexe in hohen Ausbeuten. Bei Anwesenheit neutraler mono- oder bidentater Donoren in Lösung entstehen 1 : 1-Addukte der gemischten Komplexe. Die Komplexe wurden mittels Elementaranalyse, IR, Elektronen- und ESR-Spektren, sowie mittels Messungen der magnetischen Momente charakterisiert. Von einigen Komplexen wurden thermisches Verhalten (DTA) und die elektrischen Eigenschaften untersucht und mit der Struktur der Komplexe korreliert.

### **Introduction**

The chemistry of antipyrine (2,3-dimethyl-1-phenyl-5-pyrazolone) and its derivatives continues to be of considerable importance in analytical chemistry [1], in biological [2] and clinical [3] studies. Schiff base metal complexes of antipyrine have attracted special attention due to their importance in the fluorometric esti-

mation of metal ions [4]. A variety of synthetic pathways has been devised for the preparation of antipyrine complexes; the common direct method involves reaction of antipyrine with metal salts [5–10]. We now report the direct electrochemical synthesis of Co(II), Ni(II), and Cu(II) complexes of 4-aminoantipyrine Schiff bases derived from salicylaldehyde (*SAAP*) and 2-hydroxy-1-naphthaldehyde (*NAAP*) by the electrochemical oxidation of metals in non-aqueous solution of the ligands; adducts with 1,10-phenanthroline (*phen*) and triphenylphosphine (*Ph<sub>3</sub>P*) were also prepared by the same technique. The complexes were characterized by conventional physical and chemical methods.

## Experimental Part

Metal sheets (Cobalt, Nickel, and Copper), (Alfa) were first treated with conc. nitric acid to remove any surface film, and then washed repeatedly with distilled water, after which the dried metal was lightly abraded with fine sand paper and polished with tissue. Acetone was dried over anhydrous magnesium sulphate.

The electrochemical procedure followed the one described by Tuck et al. [11–20] and other authors [21–25]. The anode, in the form of a sheet (2 × 2 cm) was suspended via copper wire in the solution in a 100 ml-tall form beaker. The cathode was a platinum wire (5 cm long and 1 mm diameter) and the cell was of the general form  $M(+)/\text{Acetone} + R(\text{OH})/\text{Pt}(-)$ . The applied voltage, 20–25 V, gives a current of 20 mA which produced a reasonable rate of reaction without overheating the solution.  $\text{Et}_4\text{NClO}_4$  (ca. 25 mg) was used as supporting electrolyte and generally enhanced the conductivity of the solution. The solution composition, electrochemical conditions and yields are given in Table 1. Some typical procedures are described in detail below. Analytical results are given in Table 2.

### *Electrochemical Synthesis of [Cu(OR)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (Complex No. 7)*

In a typical experiment, the electrochemical oxidation of a copper anode in a solution phase of 50 ml acetone, 0.61 g of *SAAP*(*ROH*) and 25 mg  $\text{Et}_4\text{NClO}_4$  for 2.5 h at 25 V and a current of 20 mA led to the dissolution of 64 mg of copper. In a separate experiment, the electrochemical efficiency  $E_f$  (mole of metal dissolved per Faraday of charge) was found to be 0.53 mol  $\text{F}^{-1}$ . The reaction mixture was filtered to remove the excess metal particles and the filtrate was slowly evaporated; the resulting brown powder was washed several times with ether and dried in vacuo. The separated complex (0.63 g, 90%) was identified as  $[\text{Cu}(\text{OR})_2(\text{H}_2\text{O})_2]$ . The other metal complexes were prepared by the same procedure, in yields of 85% or more (see Table 1).

### *Electrochemical Synthesis of [Cu(OR)<sub>2</sub>phen]2H<sub>2</sub>O (Complex No. 8)*

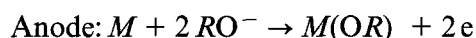
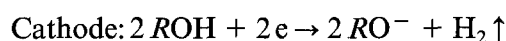
Electrolysis of copper into a solution of 0.46 g  $R(\text{OH})_2$ , 0.14 g 1,10-phenanthroline and 25 mg  $\text{Et}_4\text{NClO}_4$  in 50 ml acetone for 2 h at 20 V and 20 mA current led to dissolution of 50 mg copper ( $E_f = 0.52$  mol  $\text{F}^{-1}$ ). The brown crystals which formed in the cell during the experiment were removed by filtration and washed successively with acetone and ether. The reddish brown product (0.65 g, 93% based on the metal dissolved) was identified as  $[\text{Cu}(\text{OR})_2\text{phen}]2\text{H}_2\text{O}$ . When the solution contained both  $R(\text{OH})_2$  and  $\text{Ph}_3$ , the product – which was precipitated, collected and then dried in the same manner – was the appropriate 1 : 1 adduct.

The working procedure and the apparatus utilized for investigation of the solid complexes were the same as given before [15, 26].

## Results and Discussion

The preparative results show that the direct electrochemical oxidation of metals in the presence of ligand solution is a one step process and a convenient and simple route to a variety of metal complexes [23, 24]. The experimental conditions for obtaining the isolated complexes are listed in Table 1 and their analytical data in Table 2. They are deeply coloured, stable under atmospheric conditions, insoluble in common organic solvents but soluble in *DMSO* or *DMF*.

The yields are essentially quantitative based on the quantity of metal dissolved from the anode and most of the products are insoluble in the solution phase of the cell. Measurements of the electrochemical efficiency ( $E_f$ , mol  $F^{-1}$ ), for *M/SAAP* or *NAAP* (= *ROH*) systems (where  $M = \text{Co, Ni, or Cu}$ ) gave  $E_f = 0.5 \pm 0.04$  mol  $F^{-1}$ , and the formation of  $\text{H}_2$  at the cathode was corresponding to the following process:



**Table 1.** Experimental conditions for the electrochemical synthesis of  $M(\text{OR})_2$  compounds and adducts ( $M = \text{Co, Ni, Cu}$ )

No.	Complex	Solution Comp.		Voltage V	Current mA	Time h	Mass (mg)	$E_f$
		<i>R(OH)</i> Weight (g)	Add.					
<i>ROH = SAAP</i>								
1	$\text{Co}(\text{OR})_2(\text{H}_2\text{O})_2$	0.61	—	20	20	2.5	60	0.50
2	$\text{Co}(\text{OR})_2 \cdot \text{phen} \cdot 3 \text{H}_2\text{O}$	0.46	0.14	25	20	2.0	47	0.53
3	$\text{Co}(\text{OR})_2 \cdot \text{Ph}_3\text{P} \cdot \text{H}_2\text{O} \cdot 5 \text{H}_2\text{O}$	0.46	0.20	20	20	2.0	45	0.51
4	$\text{Ni}(\text{OR})_2 \cdot 4 \text{H}_2\text{O}$	0.61	—	25	20	2.5	55	0.50
5	$\text{Ni}(\text{OR})_2 \cdot \text{phen} \cdot 6 \text{H}_2\text{O}$	0.46	0.14	25	20	2.0	42	0.48
6	$\text{Ni}(\text{OR})_2 \cdot \text{Ph}_3\text{P} \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}$	0.46	0.20	25	20	2.0	41	0.47
7	$\text{Cu}(\text{OR})_2(\text{H}_2\text{O})_2$	0.61	—	25	20	2.5	64	0.53
8	$\text{Cu}(\text{OR})_2 \cdot \text{phen} \cdot 2 \text{H}_2\text{O}$	0.46	0.14	20	20	2.0	50	0.52
9	$\text{Cu}(\text{OR})_2 \cdot \text{Ph}_3\text{P} \cdot \text{H}_2\text{O} \cdot 4 \text{H}_2\text{O}$	0.46	0.20	25	20	2.0	48	0.50
<i>ROH = NAAP</i>								
10	$\text{Co}(\text{OR})_2(\text{H}_2\text{O})_2 \cdot 2 \text{H}_2\text{O}$	0.71	—	25	20	2.5	60	0.54
11	$\text{Co}(\text{OR})_2 \cdot \text{phen} \cdot 2 \text{H}_2\text{O}$	0.54	0.14	20	20	2.0	47	0.53
12	$\text{Co}(\text{OR})_2 \cdot \text{Ph}_3\text{P} \cdot \text{H}_2\text{O} \cdot 4 \text{H}_2\text{O}$	0.54	0.20	20	20	2.0	45	0.51
13	$\text{Ni}(\text{OR})_2 \cdot 3 \text{H}_2\text{O}$	0.71	—	25	20	2.5	54	0.50
14	$\text{Ni}(\text{OR})_2 \cdot \text{phen}$	0.54	0.14	25	20	2.0	42	0.49
15	$\text{Ni}(\text{OR})_2 \cdot \text{Ph}_3\text{P} \cdot \text{H}_2\text{O} \cdot 2 \text{H}_2\text{O}$	0.54	0.20	25	20	2.0	42	0.49
16	$\text{Cu}(\text{OR})_2(\text{H}_2\text{O})_2$	0.71	—	30	20	2.5	65	0.54
17	$\text{Cu}(\text{OR})_2 \cdot \text{phen} \cdot 4 \text{H}_2\text{O}$	0.54	0.14	25	20	2.0	51	0.53
18	$\text{Cu}(\text{OR})_2 \cdot \text{Ph}_3\text{P} \cdot \text{H}_2\text{O} \cdot 5 \text{H}_2\text{O}$	0.54	0.20	25	20	2.0	50	0.52

*phen* = 1,10-phenanthroline, *Ph*<sub>3</sub>*P* = triphenyl phosphine

**Table 2.** Analytical, magnetic moment, and infrared data of  $M(OR)_2$  compounds and adducts

No.	Microanalysis calcd. (found)			$\mu_{\text{eff}}$	Infrared spectra			
	%C	%H	%M		C=O	C=N	M-O	M-N
	ROH = SAAP				1656	1592	422	508
1	61.1(60.8)	5.1(4.9)	8.3(8.0)	4.80	1656	1592	422	508
2	63.7(63.9)	5.1(5.3)	6.5(6.3)	4.85	1650	1601	432	507
3	62.30(62.3)	5.7(5.5)	5.7(5.4)	4.90	1656	1618	434	509
4	58.2(57.9)	5.4(5.2)	7.9(7.6)	Dia.	1655	1608	432	510
5	60.1(59.9)	5.4(5.2)	6.1(5.8)	2.95	1660	1595	433	511
6	66.9(66.7)	5.3(5.2)	6.1(5.8)		1657	1595	430	510
7	60.4(61.1)	5.3(5.2)	8.9(8.6)	1.89	1660	1600	422	503
8	63.0(62.7)	5.3(5.2)	7.1(6.8)	1.80	1658	1598	432	509
9	63.1(62.8)	5.5(5.4)	6.1(5.9)		1657	1598	430	508
	ROH = NAAP							
10	62.6(62.2)	5.2(5.1)	7.0(6.8)	4.74	1648	1602	424	513
11	68.1(67.8)	4.9(4.7)	6.0(5.8)		1645	1590	425	510
12	66.3(65.9)	5.4(5.2)	5.3(5.1)		1646	1592	428	513
13	64.0(63.8)	5.1(4.9)	7.1(7.0)		1650	1590	427	510
14	70.7(70.6)	4.6(4.4)	6.2(6.1)		1652	1592	425	509
15	68.5(68.2)	5.3(5.1)	5.4(5.2)		1660	1590	430	508
16	65.3(64.8)	4.9(4.7)	7.8(7.5)	1.80	1663	1587	452	512
17	65.4(65.1)	5.1(5.0)	6.2(5.8)	1.76	1657	1592	432	507
18	64.9(64.7)	5.5(5.3)	5.6(5.3)		1666	1602	452	509

A similar mechanism can be applied for the synthesis of the adducts of metal complexes which have not been reported previously.

#### *Analysis and Spectral Studies*

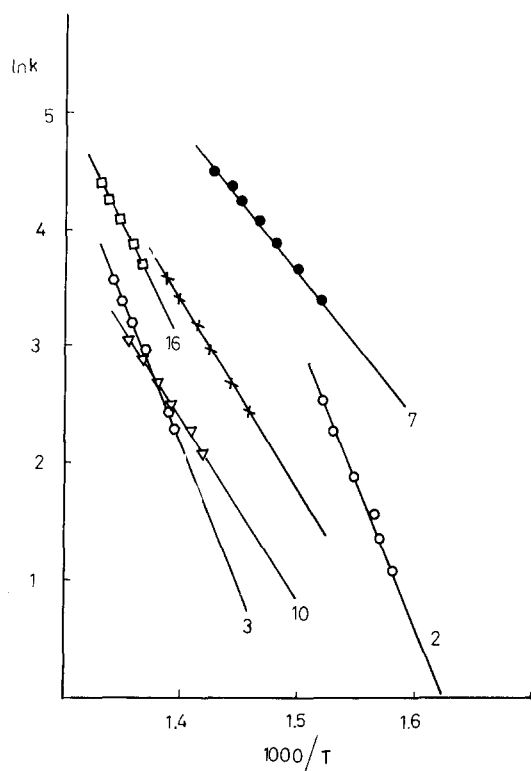
All the prepared complexes were subjected to elemental analysis; the data are listed in Table 2. The results reveal that the Schiff bases behave as monobasic bidentate ligands towards metal ions.

The IR spectra of the complexes (Table 2) provide direct information about the coordination of ligands. The IR spectra of the solid complexes compared to those of the free ligands indicate that the C=N band is shifted by 18–33  $\text{cm}^{-1}$  to lower wave numbers, hence the nitrogen atom is contributing to form a coordination bond with the metal ions. It is not possible to discuss the proton displacement from the behaviour of the  $\nu$  OH band since the complexes contain water molecules masking the phenolic bands [27]. The bands corresponding to  $\delta$  OH (1306  $\text{cm}^{-1}$  for both ligands) and  $\nu$  C-OH (1243–1269  $\text{cm}^{-1}$ ) of the free ligands disappeared on complex formation. This indicates the deprotonation of the ligands in the complexes. The C=O band does not undergo any appreciable shift in the spectra of the complexes indicating that the C=O group is not involved in coordination with the metal ions. The coordination of the Schiff base through oxygen and nitrogen

atoms to metal ions is further indicated by the appearance of  $\nu$   $M-O$  and  $\nu$   $M-N$  at  $422-452$  and  $507-513\text{ cm}^{-1}$ , respectively. The presence of the new band in the region  $850-871\text{ cm}^{-1}$  assigned to the out of plane deformation vibrations of coordinated water [28], supports the presence of the coordinated water molecules.

The data from the DTA indicate that the thermal degradation of the complexes proceeds in three steps and in addition there is another step corresponding to the loss of the second ligand molecule (*phen* or *Ph<sub>3</sub>P*). The first step consists of weak endothermic peaks within the range  $143-147^\circ\text{C}$  corresponding to the removal of water molecules. The second step corresponds to the phase transformation and lies within the temperature range  $220-239^\circ\text{C}$  with a medium exothermic peak. The third step which is characterised by strong exothermic peaks within the  $440-544^\circ\text{C}$  range represents the final decomposition of the complexes to metal oxide. The energies of activation ( $E_a$ ) of the decomposition processes have been evaluated from the DTA curves [29-31]. The thermal decomposition follows a first order kinetic law for which the rate constant ( $K$ ) is obtained from the DTA curves at certain temperature ( $T$ ). Arrhenius plots were then constructed and the energy of activation was obtained from the slopes (shown in Fig. 1).

The cobalt(II) complexes have magnetic moments (Table 2) which lie in the range reported for octahedral structures [32]. The Nujol mull spectra show two bands within the ranges  $14706-16286$  and  $18868-20833\text{ cm}^{-1}$  due to  ${}^4T_{1g} \rightarrow {}^4A_{2g}(\nu_2)$  and  ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)(\nu_3)$  transitions respectively, indicating an octahedral geometry. The  $\nu_2$  and  $\nu_3$  values are used to calculate the third transition  ${}^4T_{1g} \rightarrow$



**Fig. 1.** Arrhenius plots constructed from DTA thermograms of complexes 1-3, 7, 10, and 16. 1 ( $E=31$  kcal/mol), 2 (136), 3 (51), 7 (26), 10 (34), and 16 (53)

${}^4T_{2g}$  (F), ( $\nu_1$ ) band to be within the range  $6940-7745\text{ cm}^{-1}$  by the equation used for the  $d^7$  system [33]. The spectral parameters  $10Dq$ ,  $B$ ,  $\beta$  and  $\nu_2/\nu_1$  are calculated and found to be  $7765-8541$ ,  $827-943$ ,  $0.83-0.97$  and  $2.10-2.12$ , respectively, which is consistent with the proposed stereochemistry [33].

The electronic absorption spectrum of the nickel(II) complex (**5**) shows two bands at  $15625$  and  $25970\text{ cm}^{-1}$  assigned to the transition  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F) ( $\nu_2$ ) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (P) ( $\nu_3$ ), respectively, in octahedral structure [32]. Also the magnetic moments ( $2.95\text{ BM}$ ) provide additional evidence for the proposed structure. The  $10Dq$ ,  $B$ ,  $\beta$  and  $\nu_2/\nu_1$  are evaluated using  $d^8$  equation and are  $10070$ ,  $795$ ,  $0.73$  and  $1.55$ , respectively, which is in a good agreement with those reported for octahedral structures [34]. The Nujol mull spectrum of the diamagnetic nickel(II) complex (**4**) shows a band at  $19231\text{ cm}^{-1}$  assigned to the  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  transition in a square planar geometry [32]. The considerable reduction in the  $B$  values of the free ion on complex formation indicates the covalent character of the metal to ligand bond [35].

The Nujol mull spectra of the copper(II) complexes comprise two bands within the ranges  $15385-14706$  and  $19231-18182\text{ cm}^{-1}$  that can be assigned to the electronic transitions  ${}^2B_{1g} \rightarrow {}^2E_g$  and  ${}^2B_{1g} \rightarrow {}^2B_{2g}$ , respectively, within the energy level diagram for the copper(II) ion in a strong tetragonally elongated octahedral symmetry.

The X-band ESR spectra on polycrystalline powder of the copper(II) complexes at room temperature exhibit an intense sharp signal with two lines at  $g_{\parallel} = 2.21697-2.52702$  and  $g_{\perp} = 2.01243-2.05777$  with no obvious hyperfine struc-

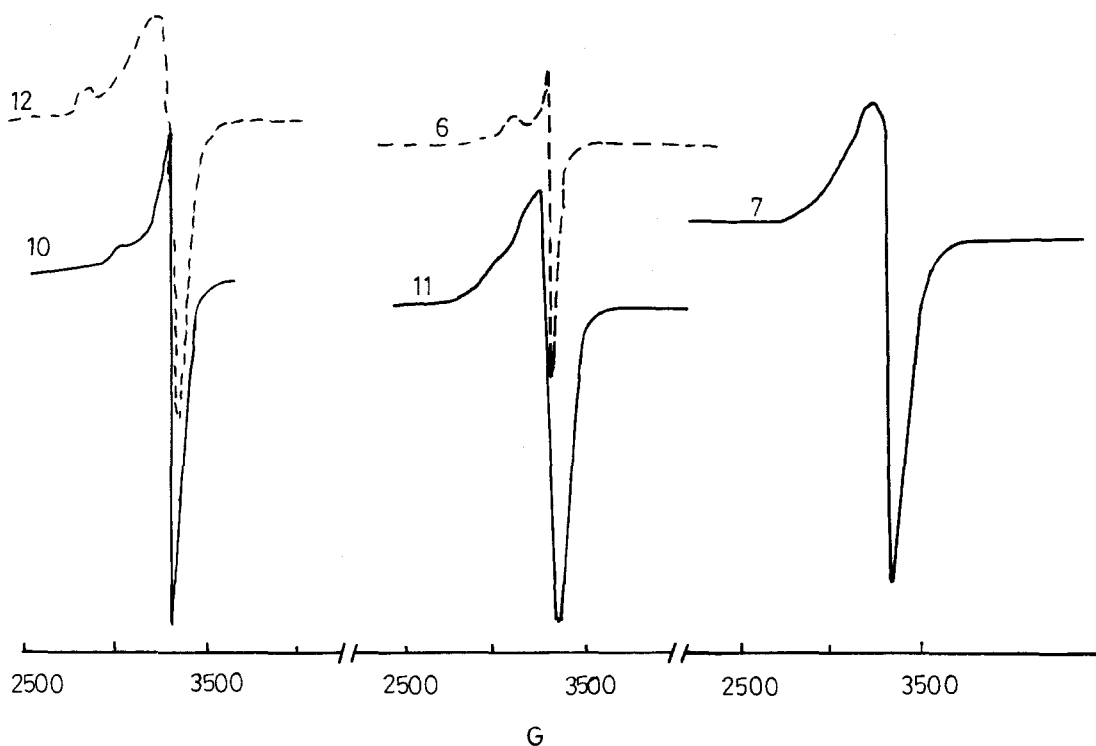


Fig. 2. X-band ESR spectra of solid complexes **6**, **7**, and **10-12**

ture (Fig. 2). The relation  $g_{\parallel} > g_{\perp}$  indicates a normal tetragonal Cu(II) ion environment [36, 37] with  $d_x^2 - y^2$  ground state with stronger interaction along the Z-axis accompanied by an increase in the value of  $g_{\parallel}$  with an increase in the length of the bond in the XY plane to decrease in turn both in-plane covalency and the energy of the  $d_x^2 - y^2$  transition. None of the complexes have sufficient small lowest  $g$  value to suggest a  $d_z^2$  ground state and hence trigonal bipyramidal environment for Cu(II) are ruled out. The  $g$ -values of copper(II) complexes can be used to derive the ground state [38]. A parameter  $G$  has been calculated by using the expression [36]:  $G = (g - 2)/(g - 2)$ . The value of  $G$  reflects the exchange interaction between copper centres in the polycrystalline complex. According to Hathaway et al. [39–41] values of  $G$  less than 4 indicate considerable exchange interaction in the solid complexes while values of  $G$  larger than 4 are typical of negligible exchange interactions, which is the case in the copper(II) complexes under investigation. The average  $g$  values are found to be in the range 2.105–2.214, i. e. above the free ion value (2.0023) which indicates strong covalency in bonding between the copper(II) ion and the ligand molecules [42].

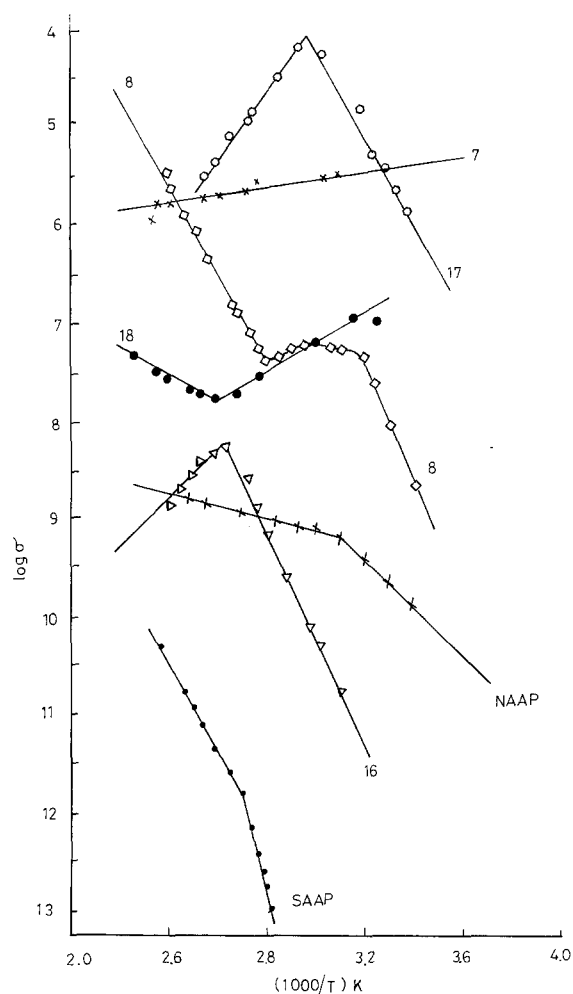


Fig. 3. Electrical resistivities of SAAP, NAAP, and their metal complexes

The electrical conductivities ( $\sigma$ ) in  $\text{Ohm}^{-1}\text{cm}^{-1}$  and the activation energies ( $\Delta E$ ) in eV of *SAAP* and *NAAP* as well as their metal complexes were obtained by applying  $\sigma = \sigma_0 \exp^{-\Delta E/KT}$ , where  $\sigma_0$  is a temperature independent conductivity constant and  $K$  is the Boltzman constant. The measurements were carried out at different temperatures in the 25–170°C range. The plot of  $\log \sigma$  versus  $1000/T$  (Fig. 3) shows that the conductivity of complexes **7** and **18** decrease as the temperature increases, which is characteristic for metallic behaviour. For complexes **8**, **16**, and **17** the reverse effect is shown, indicating semiconductor behaviour. The inflection observed in the case of most complexes except complex **7** can be attributed to a change in the conduction mechanism.

The conductivity of the Cu-*SAAP* complex is higher than that of the free ligand *SAAP*. This increase is probably due to a discontinuity of the chemical bonds existing in the complex. The conductivity of the adduct complex **8** is less than that of complex **7** indicating the effect of adducting agent. For *NAAP* complexes the adduct increases the conductivity. The decrease in the conductivity of *NAAP* complex **16** may be due to distortions in the conduction pathway through the metal caused by lattice imperfections which affect the movement of the electrons. The conductivity of the Cu-*NAAP* complex is less than that of the Cu-*SAAP* complex. This may be due to the fact that the lone pair of electrons on the phenolic oxygen atom becomes engaged in the naphthyl ring resonance more than in the phenyl ring. This lowers the electron density on the oxygen atom which subsequently decrease the electrical conductivity.

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