

## Nickel(II), Cobalt(II), Copper(II) & Palladium(II) Complexes of 1,2-Di-(*o*-salicylaldiminophenylthio) ethane

GURUCHARAN MUKHERJEE & SAILENDRA N PODDAR\*

Department of Inorganic Chemistry,  
Indian Association for the Cultivation of Science,  
Jadavpur, Calcutta 700 032

and

KAMALENDU DEY

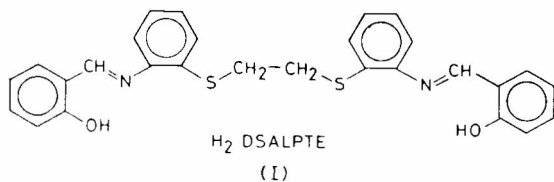
Department of Chemistry,  
University of Kalyani, Kalyani 741 235

Received 23 May 1985; revised and accepted 28 August 1985

The complexes of sexadentate ONS donor ligand, 1,2-di-(*o*-salicylaldiminophenylthio)ethane with Ni(II), Co(II), Cu(II), and Pd(II) have been prepared and characterised by elemental analyses, IR and electronic spectra, molar conductance and magnetic moment data. The results indicate that the ligand behaves either as a dianion or a neutral sexadentate one, depending on the reaction condition.

Although the sexadentate ONS donor ligand, 1,2-di-(*o*-salicylaldiminophenylthio)ethane(I) (abbreviated as H<sub>2</sub>DSALPTE) and its Co(III) complex were first reported by Dwyer *et al*<sup>1</sup> and Cannon *et al*<sup>2</sup> no further reports on the complexes of this ligand with other transition metals have come to our notice. In view of this, we report herein the synthesis and characterisation of Ni(II), Co(II), Cu(II) and Pd(II) complexes of H<sub>2</sub>DSALPTE.

The ligand (I) was prepared as reported in literature<sup>1</sup>, m.p. 173°C. (Found: C, 70.0; H, 5.2; N, 5.92. Calc. for C<sub>28</sub>H<sub>24</sub>S<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.42; H, 4.96; N, 5.79%). The ligand was characterised by its spectral data.



All the complexes isolated in the present study were prepared by the following general procedure: To an ethanolic (40 ml) suspension of H<sub>2</sub>DSALPTE (0.001 mol) was added with stirring a solution of metal acetate (0.001 mol) (in the case of Ni, Co and Cu) and of Na<sub>2</sub>PdCl<sub>4</sub> (in the case of Pd) in ethanol and refluxed for 6 hr on a water-bath. The metal complexes that precipitated out during reflux were filtered off, washed thoroughly with ethanol and dried in a vacuum desiccator over fused CaCl<sub>2</sub>.

The colour, m.ps, molar conductances, magnetic moments and analytical data are recorded in Table 1. The analytical data agree with the general formula [(MDSALPTE)] (for M=Ni(II), Co(II) and Cu(II)) and [(MH<sub>2</sub>DSALPTE)Cl<sub>2</sub>] (for M=Pd(II)).

The νOH of the free ligand at 3060, 2980 cm<sup>-1</sup> disappears in the spectra of all the complexes, except in the case of Pd(II) complex, indicating that Ni(II), Co(II) and Cu(II) complexes are formed by the deprotonation of the two phenolic -OH groups in the ligand.

The νC=N mode of the free ligand at 1615 cm<sup>-1</sup> is shifted to lower wavenumbers (Δν=5-10 cm<sup>-1</sup>) in all the metal complexes suggesting coordination of the metal ions to the azomethine nitrogen. The ν(-S-CH<sub>2</sub>) mode of the free ligand appears as a split band at 690 and 650 cm<sup>-1</sup>. However, this mode is shifted in the spectra of complexes and appears at 660-650 and 640-610 cm<sup>-1</sup> suggesting the bonding of the metal ion through sulphur atom of the ligand. This is further supported by the presence of bands at 325-305(Ni-S), 365-240(Co-S), 470-370 (Cu-S) and 385-295 cm<sup>-1</sup> (Pd-S) in the far IR spectra of the complexes<sup>4-6</sup>. The νC-S mode of the ligand at 785 cm<sup>-1</sup> is also shifted by about 30-35 cm<sup>-1</sup> in the complexes indicating M-S linkage (M=Ni, Co, Cu, Pd).

The νC-O of the free ligand at 1370 cm<sup>-1</sup> is shifted to lower wavenumbers (Δν=10-25 cm<sup>-1</sup>) in Ni(II), Co(II) and Cu(II) complexes, suggesting M-O linkage. However, in the Pd(II) complex no lowering of νC-O mode is observed, suggesting that Pd-O bonding is absent.

Linkage through N and O donor atoms in the case of Ni, Co, and Cu complexes is also supported<sup>4,5</sup> by bands at 510-415 (νNi-N+νNi-O), 560-420 (νCo-N+νCo-O), and 570-530 cm<sup>-1</sup> (νCu-N+νCu-O). Bands at 485-420 cm<sup>-1</sup> for Pd(II) complex can be assigned<sup>4</sup> to νPd-N.

The molar conductances of Ni(II), Co(II) and Cu(II) complexes indicate their non-electrolytic nature in solution (Table 1). Palladium(II) complex behaves as a 1:2 electrolyte in solution<sup>7</sup>.

The room temperature magnetic moments of the complexes (Table 1) suggest octahedral structures for all the complexes except the Pd(II) complex.<sup>7</sup> The magnetic moment of Co(II) complex is lower than the expected value of 3.6 B.M. Similar abnormal value has been reported for a pseudo-octahedral Co(II) complex<sup>8</sup>.

The electronic spectra in solution also agree with the pseudo-octahedral geometry of the complexes [except Pd(II) compound]. [Ni(DSALPTE)] shows three

Table I – Colour, Conductivity, Magnetic Moments and Analytical Data

Compound	Colour	$\Lambda^a$ ( $\text{cm}^2\text{mol}^{-1}$ )	$\mu_{eff}$ (B.M.) at 298 K ( $\pm 0.05$ B.M.)	Found (Calc)%					m.p. ( $^{\circ}\text{C}$ )
				C	H	N	M	Cl	
Ni(DSALPTE) (1)	Purple	7.7 <sup>b</sup>	3.31	62.2 (62.14)	4.17 (4.07)	5.07 (5.18)	10.77 (10.86)	—	>250 $^{\circ}\text{C}$
Co(DSALPTE) (2)	Deep brown	30.4 <sup>b</sup>	2.86	61.9 (62.12)	3.98 (4.07)	5.25 (5.17)	11.06 (10.88)	—	>250 $^{\circ}\text{C}$
Cu(DSALPTE) (3)	Green	0.63 <sup>c</sup>	1.91	51.78 (51.59)	4.55 (4.03)	5.55 (5.13)	11.3 (11.64)	—	146 $^{\circ}\text{C}$
[Pd(H <sub>2</sub> gSALPTE)] <sup>-</sup> Cl <sub>2</sub> (4)	Orange	97.3 <sup>d</sup>	Diamagnetic	50.70 (50.80)	3.27 (3.32)	4.10 (4.7)	17.10 (18.08)	10.50 (10.88)	>215 $^{\circ}\text{C}$

<sup>a</sup> Molar conductivity of  $10^{-3}$  to  $5 \times 10^{-4} M$  solutions; <sup>b</sup> measured in MeOH; <sup>c</sup> measured in nitrobenzene; and <sup>d</sup> measured in DMSO

bands at 455, 307 and 272(sh) nm. The band due to  $^3A_{2g} \rightarrow ^3T_{2g}$  transition which should occur around 1000 nm could not be detected since the spectra could only be recorded in the region 800-200 nm. Based on octahedral geometry, the 455 nm band has been assigned to  $^3A_{2g} \rightarrow ^3T_{1g}$  and 307 nm band to  $^3A_{2g} \rightarrow ^3T_{1g}(P)$  transitions<sup>9</sup>. However, slight deviations from the reported band maxima in an ideal Ni(II) compound is possible due to the distortion of the overall geometry in the complexes under consideration. Similarly, based on the same geometry, the bands at 566 and 406 nm in the Co(II) complex may be assigned to  $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$  and  $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$  transitions respectively<sup>9</sup>. The green Cu(II) complex, [Cu(DSALPTE)] shows only one band at 396 nm. This is consistent with an octahedral  $d^9$ -system with considerable Jahn-Teller distortion. It is also reported that the green or blue Cu(II) complexes are usually tetragonally distorted<sup>10</sup>. So it is plausible that the Cu(II) complex has distorted octahedral geometry.

The Pd(II) complex, [Pd(H<sub>2</sub>DSALPTE)]Cl<sub>2</sub> shows strong bands in the UV region with a shoulder at 460 nm. This may be tentatively assigned to  $^1A_{1g} \rightarrow ^1E_g$

transition in square planar geometry<sup>9</sup>. However, completely satisfactory interpretation is still lacking for such type of complexes.

One of us (K D) is grateful to DST, Govt. of India for research grant.

#### References

- 1 Cannon R D, Chiswell B & Venanzi L M, *J chem Soc (A)*, (1967) 1278.
- 2 Dwyer F P, Gill N S, Gyrfas E C & Lions F, *J Am chem Soc*, **76** (1954) 383.
- 3 Bellamy L J, *The infrared spectra of complex molecules*, 3rd Edn (Chapman & Hall, London), 1975.
- 4 Bhav N S & Kharat R B, *J inorg nucl Chem*, **43** (1981) 414.
- 5 Tarafder M T H, Jalil Miah M A & Bose R N, *J inorg nucl Chem*, **43** (1981) 3151.
- 6 Nakamoto K, *Infrared and Raman spectra of inorganic and coordination compounds* (John Wiley, New York) 1978.
- 7 Geary W J, *Coord chem Rev*, **7** (1971) 81.
- 8 Barefield E K, Busch D H & Nelson S M, *Quart Rev*, **22** (1968) 457.
- 9 Lever A B P, *Inorganic electronic spectroscopy* (Elsevier, Amsterdam), 1968.
- 10 Cotton F A & Wilkinson G, *Advanced inorganic chemistry*, 3rd Edn (Wiley-Eastern Ltd), 1972.