

TABLE 1—CHARACTERISATION DATA OF NICKEL(II) MIXED CHELATES (DRIED AT 120°C)

Chelates	Colour	Ni (%)		N(%)	
		Found	Calc.	Found	Calc.
[Ni(dipy)(sal) ₂]	Green	12.6	12.8	6.2	6.1
[Ni(o-phen)(sal) ₂]	Yellowish green	12.3	12.2	5.4	5.8
[Ni(dipy)(5-Cl-sal) ₂]	Green	10.9	11.2	5.1	5.3
[Ni(o-phen)(5-Cl-sal) ₂]	Yellowish green	10.8	10.7	5.1	5.1
[Ni(dipy)(5,6-benzosal) ₂]	Light green	10.3	10.5	5.1	5.0
[Ni(o-phen)(5,6-benzosal) ₂]	Brownish green	9.9	10.1	4.7	4.8
[Ni(dipy)(hac) ₂]	Green	11.9	12.1	5.5	5.8
[Ni(o-phen)(hac) ₂]	Yellowish green	11.6	11.5	5.3	5.5

Some of the air dried hydrated compounds were analysed for carbon, hydrogen (at C.D.R.I., Lucknow) and lattice water with satisfactory results.

TABLE 2—MAGNETIC MOMENT, CONDUCTIVITY AND ELECTRONIC SPECTRA OF NICKEL(II) MIXED CHELATES

Chelates	Magnetic moment (B.M.)	Conductivity in methanol (ohms ⁻¹ cm ² mole ⁻¹)	$\nu_1(\epsilon)=10Dq$, kK	$\nu_2(\epsilon)$, kK	ν_2/ν_1
[Ni(dipy)(sal) ₂]H ₂ O	3.19	2	10.20 ^a	16.7 ^a	1.64
[Ni(o-phen)(sal) ₂]1.5H ₂ O	3.20	1	10.21(12.9) ^b	16.66(24.2) ^b	1.63
[Ni(dipy)(5-Cl-sal) ₂]H ₂ O	3.19	1	10.21(9.3) ^b	16.66(13.9) ^b	1.63
[Ni(o-phen)(5-Cl-sal) ₂]1.5H ₂ O	3.24	1	10.21(11.0) ^b	16.66(20.8) ^b	1.63
[Ni(dipy)(5,6-benzosal) ₂]	3.17	2	10.60 ^a	17.20 ^a	1.23
[Ni(dipy)(hac) ₂]1.5H ₂ O	3.20	1	—	16.94(7.2) ^c	—

a=nujol mull ; b=chloroform ; c=ethanol.

certainty because of the high absorption of the heterocyclic donors. The spin-forbidden transition ${}^3A_{2g}(F) \rightarrow {}^1E_g$ could be detected in solution spectra in the region 11.3-13.2 kK (ϵ 3.0-8.5). The $\nu_2 : \nu_1$ ratios of the mixed chelates are around 1.62 indicating the pseudooctahedral nature of the chelates⁸. The 10 Dq ($=\nu_1$) values are consistent with the 10 Dq values of other [NiN₂O₄] chromophores (e.g. [Ni(tmen)(tfa)₂]⁹ : 10 Dq=9.8 kK ; tmen=N, N, N¹, N²-tetramethyl ethylenediamine and tfa=trifluoroacetylacetate ion).

The infrared spectrum of [Ni(dipy)(sal)₂] registers band at 1613 ($\nu_{C=O}$)¹⁰, 1580 cm⁻¹ (ν_{C-O})¹¹ and 740 cm⁻¹ (ν_{dipy}). The $\nu_{C=O}$ band of [Ni(H₂O)₂-(sal)₂] appears at 1640 cm⁻¹ and a typical dipyriddy band of [Ni(OH₂)Cl(dipy)₂]Cl.2H₂O shows up at 740 cm⁻¹. Thus we are convinced that in these mixed chelates we have both the hydroxyaldehyde and the heterocyclic donors coordinated to nickel(II).

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Mixed Ligand Complexes. Part IX.

Methioninato bis(biguanide) Cobalt(III) Salts

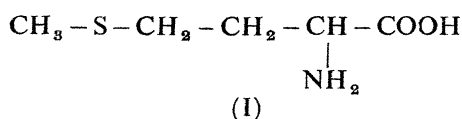
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MMETHIONINE(1) is a flexidentate ligand being capable of chelating as a tridentate (SNO) and bidentate(SN) and (NO) donors. Preparation and properties of the mixed chelate [Co(meth)(BigH)₂]²⁺ (meth H=methionine) were undertaken to ascertain the donor sites. Attempts to synthesise

the mixed chelate containing cysteine and biguanide ended in failure.



Experimental

Biguanide acid sulphate¹ and *cis*-diammine *bis*(biguanide) cobalt(III) base² were prepared by published procedures. Aminoacidato *bis*(biguanide) cobalt(III) compounds³ were also obtained by procedures developed in this laboratory (α -alanH = alanine; valinH = valine; leucH = leucine).

dl-Methioninato *bis*(biguanide) cobalt(III) iodide :

Cis-diammine *bis*(biguanide) cobalt(III) base (0.003 mol) in water (20 ml) was allowed to react with *dl*-methionine (0.003 mol) on a steam bath for forty minutes. After ammonia evolution had ceased the solution was filtered and neutralised with HCl (1 : 3) followed by the addition of KI (~1 gm). The solution was then allowed to stand overnight at room temperature. The separated red-violet crystals were further purified from hot water. (Found : Co, 8.8; N, 22.8; I, 37.1; H₂O, 2.7%. Calc. for [Co(*dl*-meth)(BigH₂)₂]₂·I₂·H₂O : Co, 8.7; N, 22.6; I, 37.3; H₂O, 2.6%).

dl-Methioninato *bis*(biguanide) cobalt(III) sulphate :

The above reaction mixture was neutralised with 10% H₂SO₄. The solution was concentrated to 10 ml and on cooling in a refrigerator reddish violet crystals separated. These were triturated with a little hot water, filtered and washed with alcohol. Found : Co, 11.8; N, 30.7; SO₄, 19.0%. Calc. for [Co(*dl*-meth)(BigH₂)₂]₂SO₄·H₂O : Co, 11.7; N, 30.5; SO₄, 19.0%.

l-Methioninato *bis*(biguanide) cobalt(III) sulphate :

l-Methionine and *cis*-diammine *bis*(biguanide) cobalt(III) base were reacted as described above and the solution was neutralised with H₂SO₄. The sparingly soluble sulphate salt was recrystallised from a large volume of hot water. Found : Co, 11.2; N, 29.3; SO₄, 18.7; H₂O, 3.5%. Calc. for [Co(*l*-meth)(BigH₂)₂]₂SO₄·H₂O : Co, 11.3; N, 29.5; SO₄, 18.4; H₂O, 3.4%.

Elemental analyses were done by following standard methods. Equivalent weight was determined with the aid of H⁺ form cationexchanger (IR-120) column⁸. Conductance was determined with a Philips Bridge at 0.001M. Spectra of aqueous solutions were run in 1 cm cell over the range 320-600 nm in a Hilger Uvispek Spectrophotometer.

Results and Discussion

Molar conductance of [Co(*dl*-meth)(BigH₂)₂]₂·I₂·H₂O in water was found to be 211 ohms⁻¹ cm² mole⁻¹ being in the expected range of bi-univalent electrolytes⁴. Its equivalent weight (339) was close to the required value (340). The electronic spectrum⁵ of this complex was extremely close to those of [Co(*dl*- α -alan)(BigH₂)₂]₂²⁺, [Co(*dl*-valin)(BigH₂)₂]₂²⁺, [Co(*l*-leuc)(BigH₂)₂]₂²⁺ in respect of spectral profile, band positions and molar extinction coefficients :

	¹ A _{1g} → ¹ T _{1g} (ϵ_{max})	¹ A _{1g} → ¹ T _{2g} (ϵ_{max})
[Co(<i>dl</i> -meth)(BigH ₂) ₂] ₂ ²⁺	20.41(165) (kK)	27.90(214) (kK)
[Co(<i>dl</i> - α -alan)(BigH ₂) ₂] ₂ ²⁺	20.41(155)	27.78(187)
[Co(<i>dl</i> -valin)(BigH ₂) ₂] ₂ ²⁺	20.62(161)	27.78(199)
[Co(<i>l</i> -leuc)(BigH ₂) ₂] ₂ ²⁺	20.41(144)	27.78(78)

The properties of [Co(*l*-meth)(BigH₂)₂]₂²⁺ are also comparable to those of [Co(*dl*-meth)(BigH₂)₂]₂²⁺. It is thus clear that the above mixed chelates have [CoN₆O] chromophore i.e. methionine functions as a bidentate NO donor. The sulphur end of methionine remains unattached to cobalt(III). In the mixed chelate [Co(cys)(en)₂]⁺ (cysH₂ = cysteine; en = ethylenediamine) the cysteinate ligand has been shown to be attached to cobalt(III) as an SN bidentate donor⁶. The ¹A_{1g} → ¹T_{1g} transition appears at a lower energy (16.7 kK).

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Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes of Acrylamide

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A MIDES and lactams have invoked lot of interest as ligands in recent years, since in addition to the carbonyl group, these molecules possess an amine group as a potential donor site. Further, these