Asian Journal of Chemistry Vol. 10, No. 3 (1998), 541–548

Characterisation, X-ray Diffraction and Microbiological Studies on Some [M(II) $(Phen)_x$] $TeO_3 \cdot nH_2O$ Complexes

MISS CHITRA GUPTA and R.K. GAUTAM*
Department of Chemistry
Dr. Hari Singh Gour Vishwavidyalaya, Sagar-470 003, India

Co(II), Ni(II) and Cu(II) complexes of 1,10-phenanthroline with new anion tellurite (TeO_3^{2-}) have been synthesised and characterised on the basis of elemental analysis, infrared, electronic spectra, TGA and X-ray diffraction studies. Powder X-ray diffraction studies have been undertaken to determine lattice parameters, *viz.*, crystal system, crystal lattice edge and volume. Octahderal structure for the Ni(II) and Co(II) complexes and a square-plan structures for the Cu(II) complexes have been suggested. The complexes of the series exhibit promising antibacterial and antifungal activity.

INTRODUCTION

In our previous papers[1–4] we have reported the complexes of Co(II), Ni(II) and Cu(II) with en, pn, dien, bipy and phen having MoO_4^{2-}, WO_4^{2-} and VO_3^- anion. In this paper we report three new complexes of cobalt(II), nickel(II) and copper(II) with 1,10-phenanthroline (phen) having a new anion tellurite (TeO_3^{2-}). The complexes were characterised by analytical and spectral studies.

EXPERIMENTAL

The starting materials nickel tellurite[5], cobalt tellurite[6] and copper tellurite[7, 8] were prepared by the reported method. The $M(II)L_xTeO_3 \cdot nH_2O$ were isolated by shaking $M(II)TeO_3 \cdot nH_2O$ (0.01 mol) with the required ligand (where L = 1,10-phenanthroline) (0.03 mol) in water (*ca.* 100 mL). The complexation was marked by change in colour. The products were filtered, washed 3–4 times with ether and dried in vaucum over P_4O_{10} before analysis. Nickel was estimated gravimetrically[9] as nickel dimethyl glyoxime, cobalt volumetrically[9], copper as cuprous thiocyanate[9] and tellurite gravimetrically[9] as tellurium. C, H and N were analysed at BARC, Mumbai. Infrared spectra (KBr) were recorded at CAT, Indoreo. Electronic spectra were recorded on a Chemito 2500 UV-Vis Recording Spectrophotometer at FSL, Sagar. Conductance was measured at 30°C in water using conductivity bridge. X-Ray diffraction and thermogravimetric analysis were performed at RSIC Nagpur. The weight loss was measured from room temperature up to 900°C at a heating rate of 10°C per min.

Microbiological studies

The complexes were screened for antibacterial and antifungal activity using standard paper disc method of Raper *et al.*[10] at a concentration of 50 $\mu g\ mL^{-1}$ using bacteriological nutrient agar for bacteria and Sabouraud dextrose broth and

Sabouraud dextrose agar for fungi. The antimicrobial activities of all complexes were evaluated against some gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative (*Salmonella typhi* and *Escherichia coli*) bacteria and some fungi (*Candida albicans, Chrysosporium pannicale, Trichoderma viridae* and *Rhizopus stolonifer*). The results were compared with the standard, *i.e.* norfloxacin (100 $\mu g\ mL^{-1}$) for antibacterial and clotrimazole (100 $\mu g\ mL^{-1}$) for antifungal studies. All the experiments were carried out in triplicate and the zones of inhibition were measured.

RESULTS AND DISCUSSION

The complexes are soluble in water and common organic solvents. The elemental analyses and the molecular formula of complexes are presented in Table 1

TABLE-1
ANALYTICAL DATA OF METAL-COMPLEXES

Complexes	Colour	m.w.	Analysis %: Found/Calculated				
			Metal	Te	C	H	N
$Ni(C_{12}H_8N_2)_3TeO_3\cdot 6H_2O$	Pink	864.99	6.74	14.75	49.09	3.96	9.71
			(6.64)	(14.45)	(14.96)	(4.08)	(9.52)
$Co(C_{12}H_8N_2)_3TeO_3\cdot 4H_2O$	Brown	847.22	8.13	15.06	51.92	3.56	10.34
			(7.95)	(14.85)	(51.03)	(3.80)	(9.92)
$Cu(C_{12}H_8N_2)_2TeO_3\cdot H_2O$	Green	869.85	10.30	20.98	46.69	2.88	8.98
			(10.28)	(20.66)	(46.63)	(2.91)	(9.06)

The molar conductance values of solutions of the complexes dissolved in water were measured at 10^{-3} M concentratio. These values indicate that all the complexes are electrolytes.

Electronic Spectra

Electronic spectral data of the Ni(II) complex exhibit three d-d transitions in the electronic spectrum. Among these the lowest frequency transition occurs at the end of visible region. The Ni(II) complex reveals three peaks around 12,659 cm^{-1}, 19,380 cm^{-1} and 27,778 cm^{-1} due to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ transitions respectively.[11] The spatial arrangement of the ligend atoms around the Ni(II) ion is octahedral.[12, 13] But the electronic spectra of the Co(II) complex are characterised by one band at 23,202 cm^{-1} due to $^4A_{2g}(F) \rightarrow 4T_{1g}(F)$ transition.[11, 14, 15] In the case of octahedral geometry, the transition of two electrons is forbidden which gives a weak band very close in octahedral geometry. The spectr of Cu(II) complex show only one broad medium intensity band at 14,793 cm^{-1} which may be due to the transition of $^2B_{1g} \rightarrow 2A_{1g}$ suggestive of its square planarity.[11, 16] It is belelived that it is a composite band involving transition of electrons from different occupied d-orbitals to the $d_{x^2-y^2}$ orbitals.

IR Spectra

The band assignments of the spectra are based upon infrared studies (Table-2) of $\mathrm{M(II)(Phen)_xTeO_3\cdot nH_2O}$ complexes where M(II) = Ni(II), Co(II) and Cu(II); Phen = 1,10-phenanthroline.

TABLE-2
INFRARED SPECTRAL DATA ($\mathrm{cm^{-1}}$) OF 1,10-PHENANTHROLINE COMPLEXES OF $[\mathrm{M(II)L_{3TeO_3}\cdot nH_2O}]$

Complexes	ν(OH)	$\delta_{(O-H)}$	$\nu_{(C=C)}$	$\nu_{(C=N)}$	$\nu_{(C-N)}$	$\nu_{(C-C)}$	$\nu_{(Te-O)}$	$\nu_{(M-N)}$
Phenanthroline	—	—	1584m	1558m		850m		
$\mathrm{Ni(II)L_3TeO_3\cdot 6H_2O}$	3401br	1625m	1585vs	1515m	1099m	849w	695vs	617s
$\mathrm{Co(II)L_3TeO_3\cdot 4H_2O}$	3396br	1623m	1585vs	1560m	1091m	849s	720vs	618s
$\mathrm{Cu(II)L_2TeO_3\cdot H_2O}$	3385br	1623m	1584vs	1560m	1108m	851m	700vs	618s

The complexes show a broad band around *ca.* 3400 $\mathrm{cm^{-1}}$ due to OH stretching and a sharp band at *ca.* 1620 $\mathrm{cm^{-1}}$ due to H—O—H bonding indicating the presence of water of crystallisation.[17, 18] The complexes of phenanthroline exhibit varied patterns of splitting and sometimes shifts of ligand bands apart from intensity changes in them as an indication of coordination of the ligand[19, 20] to the metal ions. In the free phen molecule strong interactions between C═C and C═N vibration give rise to two groups of doublets (1580, 1550 $\mathrm{cm^{-1}}$ and 1460, 1423 $\mathrm{cm^{-1}}$). These bands undergo remarkable changes due to coordination and new bands are found to appear in the spectra of complexes at *ca.* 1585 and *ca.* 1560 $\mathrm{cm^{-1}}$ confirming the coordination nature of phenanthroline ligand. The most important and significant band in the region *ca.* 618 $\mathrm{cm^{-1}}$ (not present in the ligand) has been assigned to ν(Te—O) mode.

Thermal Analysis

Since the IR spectra of the complexes indicate the presence of water molecules, thermal analyses were undertaken to ascertain their nature. All the complexes follow an identical pattern of thermal decomposition.

X-Ray Analysis

X-ray diffraction studies have been carried out with a view to finding out the type of crystal system, lattice parameters, cell volume and crystalline size of the complexes. The general procedure and details of the method of calculation are based on published work.[21–24] The calculated values of hkl along with d spacing (in Å), relative intensities and observed angle have been evaluated. A complete XRD data for $\mathrm{M(II)L_3TeO_3\cdot nH_2O}$ complexes, where M(II) = Ni(II), Co(II) and Cu(II), L = 1,10-phenanthroline, is given in Tables 3–6 as a representative system. In these tables however only some representative main peaks and their corresponding values have been included. These complexes have been found to form an orthorhombic system.

TABLE-3

X-RAY DATA OF $[Ni(Phen)_3TeO_3\cdot 6H_2O]$

Peak No.	Angle 2θ	d-value	Rel. Int.[%]	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (cal.)	hkl
1.	7.990	13.8945	17.6	0.004850	0.004659	(110)
2.	9.650	11.5086	12.7	0.007075	0.007072	(002)
3.	10.280	10.8051	4.3	0.008020	0.008028	(020)
4.	11.820	9.4014	10.7	0.010602	0.010610	(200)
5.	12.395	8.9668	18.1	0.011650	0.011730	(112)
6.	12.775	8.7011	8.6	0.012377	0.012378	(201)
7.	13.870	8.0172	14.0	0.014570	0.014385	(211)
8.	14.460	7.6917	9.6	0.015830	0.015912	(003)
9.	14.975	7.4286	8.9	0.016980	0.017682	(202)
10.	15.745	7.0674	28.0	0.018760	0.018638	(220)
11.	15.940	6.9815	38.5	0.019225	0.019680	(212)
12.	16.345	6.8097	15.3	0.020200	0.020406	(221)
13.	17.075	6.5206	2.8	0.022000	0.022400	(131)
14.	18.035	6.1761	15.7	0.024560	0.023940	(023)
15.	18.595	5.9917	14.4	0.026100	0.026590	(123)
16.	19.375	5.7526	7.6	0.028310	0.028280	(004)
17.	20.380	5.4717	10.4	0.031290	0.030940	(104)
18.	20.930	5.3295	10.0	0.032991	0.032951	(312)
19.	21.675	5.1484	10.4	0.035350	0.035740	(232)
20.	24.395	4.5817	6.7	0.044640	0.044580	(233)
21.	25.050	4.4637	9.3	0.047030	0.046926	(224)
22.	25.390	4.4049	13.1	0.048290	0.048024	(043)
23.	25.700	4.3526	17.6	0.049460	0.049510	(402)
24.	27.110	4.1302	10.7	0.054930	0.054880	(125)
25.	28.355	3.9523	29.8	0.059989	0.059899	(152)
26.	29.275	3.8307	5.6	0.063850	0.063640	(006)
27.	30.020	3.7377	9.3	0.067070	0.678500	(252)
28.	32.220	3.4886	6.4	0.076990	0.766720	(161)
29.	33.170	3.3914	7.9	0.081470	0.081710 0.081620	(036) (442)
30.	33.735	3.3362	9.6	0.084192	0.084230	(513)
31.	36.435	3.0964	7.9	0.097730	0.097890	(361)
32.	39.465	2.8671	1.9	0.113990	0.113820	(056)
33.	40.650	2.7869	4.5	0.120640	0.121180	(028)
34.	42.805	2.6527	1.9	0.133160	0.133740	(711)
35.	57.870	2.1744	100.0	0.234070	0.234660	(737)

A = 0.0026525, B = 0.002007, C = 0.001768, a = 18.79562 Å, b = 21.607805 Å, C = 23.022008 Å, Cell volume = 9349.9763 $Å^3$, n = 19, D_{obs} = 2.8964 gm cm^{-3}, D_{cal} = 2.91860 gm cm^{-3}

TABLE-4
X-RAY DATA OF [$CoL_3TeO_3 \cdot 5H_2O$]

Peak No.	Angle 2θ	d-value	Rel. Int (%)	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (Cal.)	hkl
1.	5.285	20.9965	6.2	0.002125	0.00212	(100)
2.	7.575	14.6545	10.8	0.004363	0.00462	(101)
3.	9.660	11.4967	17.4	0.007080	0.00757	(111)
4.	10.555	10.5243	25.0	0.008460	0.00848	(200)
5.	12.485	8.9024	8.8	0.011820	0.01180	(020)
6.	13.605	8.1726	8.8	0.014000	0.01430	(021)
7.	16.305	6.8263	14.9	0.020100	0.02028	(220)
8.	18.045	6.1727	17.8	0.024590	0.02453	(311)
9.	19.070	5.8438	2.8	0.027440	0.02757	(113)
10.	21.695	5.1437	13.3	0.035410	0.03503	(230)
11.	25.095	4.4558	23.0	0.047200	0.04720	(040)
12.	25.385	4.4057	18.2	0.048270	0.04822	(421)
13.	27.425	4.0836	7.3	0.056200	0.05595	(510)
14.	28.390	3.9475	33.4	0.060130	0.06028	(224)
15.	29.295	3.8281	9.1	0.063940	0.06300	(502)
16.	30.155	3.7214	57.0	0.067660	0.06730	(521)
17.	33.110	3.3973	100.0	0.081180	0.08112	(440)
18.	36.005	3.1322	6.5	0.095510	0.09533	(351)
19.	36.485	3.0923	3.9	0.098000	0.09840	(206)
20.	40.455	2.7998	7.9	0.119500	0.11860	(136)
21.	42.960	2.6436	2.0	0.134000	0.13430	(027)
22.	67.940	1.7324	1.0	0.312200	0.31108	(748)
23.	69.420	1.7000	0.6	0.324240	0.32375	(510)
24.	71.270	1.6615	40.4	0.339440	0.33843	(776)

A = 0.00212, B = 0.00295, C = 0.0025 a = 21.024051 Å, b = 17.822693 Å, c = 19.3604 Å
Cell volume = 7254.442 Å^3, n = 10, D_{obs} = 1.9924 gm cm^{-3}, D_{cal} = 1.9392 gm cm^{-3}

TABLE-5

X-RAY DATA OF [Cu(Phen.)$_2$TeO$_3$·H$_2$O]

Peak No.	Angle 2θ	d-value	Rel. In. (%)	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (cal)	hkl
1.	5.615	19.7634	45.7	0.00239	0.00239	(100)
2.	7.785	14.2598	20.1	0.00460	0.00460	(020)
3.	10.015	11.0902	38.5	0.00761	0.00761	(021)
4.	10.685	10.3966	28.2	0.00866	0.00956	(200)
5.	11.910	9.3306	38.5	0.01076	0.01071	(210)
6.	12.100	9.1846	28.2	0.01110	0.01000	(121)
7.	12.420	8.9188	10.1	0.01170	0.01204	(002)
8.	12.795	8.6876	14.9	0.01241	0.01257	(201)
9.	13.815	8.0489	39.4	0.01446	0.01443	(102)
10.	15.130	7.3529	69.6	0.01733	0.01717	(221)
11.	16.555	6.7239	21.4	0.02072	0.02079	(140)
12.	18.110	6.1508	28.2	0.02476	0.24780	(132)
13.	19.715	5.6544	1.9	0.02930	0.02948	(103)
14.	21.690	5.1449	24.7	0.03540	0.03487	(331)
15.	22.400	4.9838	9.2	0.03772	0.03780	(213)
16.	25.110	4.4532	25.3	0.04725	0.04700	(233)
17.	25.410	4.4015	24.7	0.04836	0.04859 0.04816	(430) (004)
18.	26.145	4.2798	6.5	0.05115	0.05143	(412)
19.	27.775	4.0331	26.8	0.05760	0.05772	(204)
20.	28.405	3.9455	53.4	0.06019	0.0609	(510)
21.	29.345	3.8217	14.4	0.06415	0.06435	(520)
22.	30.380	3.6944	6.5	0.06865	0.06895	(144)
23.	31.760	3.5378	3.2	0.07486	0.07427	(324)
24.	32.845	3.4240	11.9	0.07992	0.07985	(025)
25.	33.455	3.3633	23.3	0.08284	0.08224	(125)
26.	34.160	3.2959	11.4	0.08626	0.08604	(600)
27.	36.445	3.0956	20.7	0.09778	0.09791	(315)
28.	37.360	3.0224	2.1	0.10258	0.10268	(622)
29.	40.420	2.8021	5.8	0.11930	0.11907	(216)
30.	41.130	2.7558	3.2	0.12339	0.12472	(721)
31.	42.660	2.6613	7.6	0.13230	0.13375	(722)
32.	43.505	2.6121	4.9	0.13734	0.13711	(056)
33.	48.430	2.3601	1.5	0.16823	0.16838	(147)
34.	49.845	2.2972	1.9	0.17757	0.17647	(771)
35.	50.960	2.2502	3.2	0.18506	0.18573	(407)
36.	55.420	2.0818	2.3	0.21622	0.21598	(932)
37.	56.035	2.0608	1.5	0.22065	0.22068	(903)
38.	56.950	2.0304	100.0	0.22731	0.22790	(3, 13, 2)
39.	59.355	1.9551	1.9	0.24514	0.24496	(0, 1, 9)
40.	63.075	1.8507	2.7	0.27358	0.27318	(1, 15, 2)
41.	64.855	1.8052	2.3	0.28754	0.28716	(10, 0, 4)

A = 0.00239, B = 0.00115, C = 0.00301 a = 19.80092 Å, b = 28.54535 Å, c = 17.644164 Å, Cell volume = 9972.909 Å^3, n = 18, D_{obs} = 1.8456 gm cm^{-3}, D_{cal} = 1.85070 gm cm^{-3}

TABLE-6
CRYSTAL PARAMETERS AND OTHER CHARACTERISTICS OF [M(II)$L_xTeO_3 \cdot nH_2O$] COMPLEXES

Complex (Crystal system)	Crystal lattice edge			Unit volume Å^3	n	Density: Found (Calcd) (gm cm^{-3})
	a (Å)	b (Å)	c (Å)			
$NiL_3TeO_3 \cdot 6H_2O$ Orthorhombic	18.79562	21.607805	23.022008	9349.97630	19	2.8964 (2.9186)
$CoL_3TeO_3 \cdot 4H_2O$ Orthorhombic	21.024051	17.822693	19.360400	7254.44200	10	1.9924 (1.9392)
$CuL_2TeO_3 \cdot H_2O$ Orthorhombic	19.800920	28.545350	17.644164	9972.90900	18	1.8450 (1.8507)

Biological Activity

Microbial study revels that most of the complexes were poor and moderately active against different strains of bacteria and fungi (Table-7).

Maximum activity was observed in Ni(II) complex against *Salmonella typhii* and *Rhizopus stolonifer.* All the Co(II) complex tested showed poor activity against bacteria and fungi; Cu(II) complex showed moderate activity against *Bacillus subtilis*, *Salmonella typhii*, *Escherichia coli* (bacteria) and *Candida albicans* (fungi).

TABLE-7
MICROBIAL SCREENING RESULT OF COMPLEXES

Comp.	Antibacterial				Antifungal			
	A	B	C	D	E	F	G	H
$Ni(C_{12}H_8N_2)_3TeO_3 \cdot 6H_2O$	+	++	+++	+	++	++	+	+++
$Co(C_{12}H_8N_2)_3TeO_3 \cdot 4H_2O$	+	+	+	+	+	+	+	+
$Cu(C_{12}H_8N_2)_2TeO_3 \cdot H_2O$	++	+	++	++	++	+	+	+

*A = *Bacillus subtilis* B = *Staphylococcus aureus*, C = *Salmonella typhi*, D = *Escherichia coli*
E = *Candida albicans*, F = *Chrysosporium Pannicale*, G = *Trichoderma viridae* ,
H = *Rhizopus stolonifer*

Zone of inhibition: 15–20 mm (+) = poor inhibition; 20–30 mm (+ +) = moderate inhibition 30–45 mm (+ + +) = maximum inhibition.

Maximum activity was observed in Ni(II) complexes against C and H. All the Co(II) complexes tested showed poor activity against bacteria and fungi; Cu(II) complexes showed moderate activity against A, C, D (bacteria) and E (fungi)

ACKNOWLEDGEMENTS

The authors are thankful to Prof.. S.P. Banerjee, Head of the Department of Chemistry. Dr. Hari Singh Gour Vishwavidyalaya, Sagar for facilities. Thanks are also due to Ms Archana Mehta and Seema Jain (R.S.), Department of Botany and Mr. Sanmati Jain (R.S.), Department of Pharmaceutical Science, Dr. H.S. Gour Vishwavidyalaya Sagar for Microbial Studies and to the Directors CAT Indore, BARC Mumbai, FSL Sagar and RSIC Nagpur for C, H, N and spectral analyses etc.

REFERENCES

1. A.B. Khare, R.K. Gautam and O.P. Shrivastava, *J. Indian Chem. Soc.*, **63**, 660 (1996).
2. Roopa Singh and R.K. Gautam, *J. Indian Chem. Soc.*, **64**, 631 (1987).
3. Mahesh Kumar Kathal and R.K. Gautam, *J. Indian Chem. Soc.*, **67**, 95 (1990).
4. _________, *Asian J. Chem.*, **4**, 357 (1992).
5. J.C. Bailar, H.J. Emeleus, R. Nyholm, A.F. Trotman and Dickenson, Comprehensive Inorganic Chemistry, Vol. 3, p. 739 (1973).
6. J.W. Meller, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XI, p. 802 (1947).
7. Sneed, Maynared and Brasted, Comprehensive Inorganic Chemistry, Vol. II, pp. 98–9.
8. V.L. Zolotavin, *Zh. Anal. Khim.*, **2**, 364 (1947).
9. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 4th Edn., Longman, London, pp. 527, 529, 496, 509 (1978).
10. K.B. Raper, D.F. Alexander and R.P. Coghill, *J. Bacteriol.*, **48**, 630 (1944).
11. B.N. Figgis, Introduction to Ligand Field, Wiley Eastern, New Delhi, pp. 280, 281, 316 (1976).
12. L.E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).
13. Y. Tanabe and S. Sugano, *J. Phys. Soc. Jpn.*, **9**, 766 (1954).
14. Mathews and R.A. Walton, *Inorg. Chem.*, **10**, 7443 (1971).
15. A.B.P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1963).
16. _________, Inorganic Electronic Spectroscopy, Elsevier, New York, pp. 355–360 (1968).
17. P.J. Lucchesi and W.A. Glasscn, *J. Am. Chem. Soc.*, **78**, 141 (1956).
18. D.M. Adams and A. Squire, *J. Chem. Soc. A*, 1808 (1970).
19. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley (1978).
20. C.N.R. Rao, Chemical Application of Infrared Spectroscopy, Academic Press, New York (1963).
21. N.F.M. Henry, H. Lipson and W.A. Wooster, Interpretation of X-ray Diffraction Photography, p. 81 (1951); p. 179 (1959).
22. M.J. Burjer, X-ray Crystallography, Wiley, New York, p. 100 (1953).
23. H.S. Peiser, H.P. Rooksky and A. J.C. Wilson, X-ray Diffraction by Polycrystalline Materials, p. 344 (1955).
24. M.M. Woolfson, An Introduction to X-ray Crystallography, Cambridge University Press, Cambridge, p. 125 (1980).

(*Received:* 11 December 1997; *Accepted:* 17 February 1998) AJC-1435