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Biologically Active Bimetallic Complexes Formed from Acetylacetonates of Copper, Cobalt and Nickel

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A few binuclear complexes of either copper, cobalt or nickel acetylacetonates with silicon, tin, selenium and tellurium chloride were synthesized and characterized by elemental analyses, conductivity measurements, magnetic and spectral data. The binuclear complexes are 1:1 adducts and nonelectrolytes in solution. The complexes are biologically active as demonstrated by bacteriostatic, mammalian acute toxicity, and antialgal activity tests.

Introduction

β-diketones have proven to be versatile ligands for the study of the properties of coordination compounds [1–5]. Potential applications of β-diketone metal complexes in biomedicine have been discussed [6–10]. In particular, heavy metal complexes with β-diketones are known to possess bacteriocidal [11], antiviral [12], antifungal [13] and antialgal activities [14].

Even though β-diketone complexes have been intensively investigated, these complexes have not been used very often as starting materials for the synthesis of binuclear adducts. We have therefore undertaken the synthesis and characterization of a few bimetallic complexes formed from copper, nickel and cobalt acetylacetonates (β-diketone metal complexes) and tetravalent metal ions such as silicon, tin, selenium and tellurium. Furthermore, an attempt has been made to study the stereochemistry and the biological activity of the bimetallic complexes. The complexes were examined for antibacterial activity, mammalian acute toxicity and blue-green algal activity.

Experimental

All the chemicals used in this work were of reagent grade and used without further purification. Metal complexes of nickel(II), cobalt(II), and copper(II) acetylacetonates were prepared according to well established methods [15].

The bimetallic complexes were prepared by mixing the respective nickel(II), cobalt(II) or copper(II) acetylacetonates with either silicon(IV) chloride, tin(IV) chloride, selenium(IV) chloride or tellurium(IV) chloride, in dry chloroform in an equimolar ratio. The mixture was then stirred continuously for an hour and allowed to settle over-night. The bimetallic complexes were then filtered, washed with dry chloroform and dried in vacuum over P_2O_5.

Elemental analyses were carried out using standard procedures [16]. The nickel in the complexes was estimated gravimetrically as nickel dimethylglyoximate. Copper and cobalt were determined by the pyridine thiocyanate method. Tin and silicon were estimated gravimetrically as their oxides; selenium and tellurium were estimated by the thiourea method; while chlorine was determined as silver chloride.

Molar conductivities at room temperature were measured in dimethylformamide (DMF) using an Elico-CM-82 conductivity bridge with a cell having a cell constant of 0.829 cm^{-1}. All conductivity measurements were performed at room temperature using 10^{-3} M solutions of complex. The effective magnetic moment (μ_{eff}) was measured on a Guoy balance provided with a glass tube calibrated for diamagnetism. The electronic spectra from 200 nm (50,000 cm^{-1}) to 800 nm (12,500 cm^{-1}) were recorded with a Carl-Zeiss Specord uv-vis Spectrophotometer or a Shimadzu-200s Spectrophotometer using 1 cm glass curvets.

Infrared (IR) spectra were scanned on a Carl-Zeiss Specord-75 in the region 4000–400 cm^{-1} using the Nujol mull method. The spectra from 400–200 cm^{-1} were obtained on a Perkin-Elmer 5100-4367 spectrophotometer.

Pharmacological Tests

(A) Evaluation of Antibacterial Activity

The antibacterial activity of the test compounds was assayed against four bacteria: *S. aureus*, *B. sub-*

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tilis, *E. coli* and *P. vulgaris*. Among these organisms, the former two are gram-positive while the latter are gram-negative. All are regarded as pathogenic to human beings and animals except *B. subtilis*.

All media and bacterial suspensions were prepared using a method adapted from that of Cruickshank [17].

About 15–20 ml of molten nutrient agar was poured into sterile petri plates about 10 cm in diameter. After solidification of the agar, three cups (10 mm in diameter and 5 mm deep) were removed from each agar dish and fresh bacterial suspension was then uniformly spread on each cup. At this point, each of the cups was spotted three times with test solution at concentrations of 50, 100 and 200 μg/ml in dimethyl formamide (DMF). After incubating the plates at 37 °C overnight, the diameter of the zone of inhibition of the bacterial growth was then recorded.

A 5% phenol solution was tested as a positive control and DMF as solvent control each time the experiments were performed.

(B) Acute Toxicity Tests

The acute toxicity tests were performed on albino rats of either sex weighing between 80–120 gms using a procedure developed by Smith [18]. Since the complexes were not readily soluble in water, they were powdered and made into a suspension using a few drops of Tween-80. Dose levels of 10, 20, 50 and 100 mg/kg of bodyweight were selected and tested on six rats at each dose level. The animals were observed in order to evaluate gross changes in behavior, activity, and loss of righting reflex. The observations on the animals were made for the first six hours continuously, once an hour for the next six hours, once every three hours for the next eighteen hours, and then once every twelve hours for the next seven days. During the experiments the rats were allowed liberal amounts of food and water.

(C) Activity Studies on Blue-Green Algae

H. Welwitschii is a type of blue-green algae having a low level of cell organization. *H. welwitschii* is autotrophic and a strong nitrogen fixer [6, 19] growing well in artificial medium supplemented with inorganic constituents.

The laboratory clonal cultural of *H. welwitschii* was grown in Allen and Arnon's nitrogen free medium at a pH = 7.5 [20]. The medium was autoclaved and used as the basal medium throughout the study.

About 10 ml of the algal suspension from the basal medium containing a known weight of the algae was centrifuged, washed thoroughly with distilled water, and inoculated into the flasks containing the complexes at concentrations of 100, 200 and 300 μg/mL. All the cultures were maintained at room temperature and the growth of the algae was measured at ten day intervals.

Results and Discussion

Analytical and Physical Data

All complexes are colored and amorphous in nature. They are soluble in polar solvents such as dimethyl formamide (DMF) and dimethylsulfoxide (DMSO) but insoluble in the other common organic solvents. The elemental analyses show that the complexes are 1:1 adducts and the conductivity data suggest nonelectrolytic behavior. The analytical and physical data are presented in Tables I–III.

Magnetic and Electronic Data

The magnetic and electronic spectral data for copper acetylacetonate and its bimetallic complexes are found in Table I.

Copper acetylacetonate, $Cu(acac)_2$ exhibits a magnetic moment of 1.96 Bohr magnetons (B.M.). The magnetic moment is higher than that of the spin-only value of 1.73 B.M., leading to the conclusion that the complex is either tetrahedral (sp^3) or planar sp^2d [21]. Hall *et al.* have shown that the carbon atoms of the copper acetylacetonate in the solid state are distorted from the coordination plane toward an adjacent metal atom [22]. X-ray crystal structure determinations of copper(acetylacetonate) and copper(3-methylacetylacetonate) yield square-planar configurations [23, 24].

The bimetallic complexes of copper(II) β-diketonates have magnetic moments around 2.2 B.M.

$Cu(acac)_2$ exhibits a band at 15,500 cm^{-1} in the electronic spectrum whereas the bimetallic complexes all show a transition between 14,000 and 14,220 cm^{-1}. The band in the binuclear complexes is assigned to a d–d transition. The electronic spectra do not resemble the spectra of standard planar copper(II) complexes, but more closely agree with the spectra of established tetrahedral complexes [25, 26]. Based on the electronic spectra, and the increase in magnetic moment, a tetrahedral configuration around the copper atom is proposed for the binuclear complexes.

The observed magnetic moments for nickel acetylacetonate $Ni(acac)_2$ and its bimetallic complexes are all in the range 3.01 to 3.23 B.M., see Table II, which correlates with that for octahedral complexes [27]. The values are slightly higher than those expected for the spin only value for two electrons, and can be explained in terms of spin-orbit coupling [28]. The X-ray crystal structure determination yields a trimer with octahedral coordination around the nickel atom [29]. The magnetic data indicate that there is hardly any change in the stereochemistry

TABLE I. Analytical and Physical Data for Copper(II) Acetylacetonate and its Bimetallic Complexes.

Empirical formula of complex	%Cu[a]	%Cl	%M[b]	Molar cond. (ohm^{-1} cm^2 mol^{-1})	Magnetic moment (B.M.)	Electronic transition (cm^{-1})
$(C_{10}H_{14}O_4)Cu$	24.31 (24.28)			15.50	1.96	15,500
$(C_{10}H_{14}O_4)Cu\cdot SiCl_4$	15.05 (14.81)	32.76 (32.87)	6.39 (6.48)	51.03	2.20	14,200
$(C_{10}H_{14}O_4)Cu\cdot SnCl_4$	12.17 (12.24)	27.04 (27.15)	22.69 (22.75)	38.36	2.21	14,150
$(C_{10}H_{14}O_4)Cu\cdot SeCl_4$	13.08 (13.25)	29.29 (29.40)	15.98 (16.36)	46.69	2.20	14,200
$(C_{10}H_{14}O_4)Cu\cdot TeCl_4$	12.12 (12.03)	26.82 (26.96)	24.20 (24.06)	45.20	2.15	14,050

[a] Values in the parentheses are the calculated values. [b] M = Si, Sn, Se or Te.

TABLE II. Analytical and Physical Data for Nickel(II) Acetylacetonate and its Bimetallic Complexes.

Empirical formula of complex	%Ni[a]	%Cl	%M[b]	Molar cond. (ohm^{-1} cm^2 mol^{-1})	Magnetic moment (B.M.)	Electronic transition (cm^{-1})
$(C_{10}H_{14}O_4)Ni$	22.69 (22.65)			20.00	3.18	13,400 23,800 33,020
$(C_{10}H_{14}O_4)Ni\cdot SiCl_4$	13.92 (14.21)	34.82 (34.80)	6.63 (6.86)	30.00	3.01	14,000 25,050 33,200
$(C_{10}H_{14}O_4)Ni\cdot SnCl_4$	11.27 (11.22)	27.63 (27.46)	23.15 (23.01)	33.50	3.23	14,100 24,800 33,330
$(C_{10}H_{14}O_4)Ni\cdot SeCl_4$	12.15 (12.16)	29.68 (29.77)	16.48 (16.56)	47.00	3.15	14,200 25,000 33,250
$(C_{10}H_{14}O_4)Ni\cdot TeCl_4$	11.22 (11.03)	27.12 (26.99)	24.33 (24.33)	35.75	3.08	14,300 25,100 33,150

[a] Values in the parentheses are the calculated values. [b] M = Si, Sn, Se or Te.

around nickel(II) on formation of the bimetallic complexes.

The electronic spectra of the bimetallic complexes have three characteristic absorptions at 14,000, 25,000, and 33,000 cm^{-1} indicative of octahedral stereochemistry, see Table II. The first two are assigned to $^3A_{2g} \to {}^3T_{1g}(F)$, ν_2, and $^3A_{2g} \to {}^3T_{1g}(P)$, ν_3 respectively. Generally octahedral nickel(II) complexes exhibit a third transition from $^3A_{2g} \to {}^3T_{2g}$ at approximately 9000 cm^{-1}, but this could not be determined. When the splitting constant is nearly unity, the ν_2 transition appears as a well-defined doublet. This is due to the spin forbidden level ^1E_g gaining intensity through configurational interaction with the $^3T_{1g}(E)$ level [30, 31]. As a result of the presence of the two characteristic bands ν_2 and ν_3, it is concluded that the stereochemistry of the bimetallic complexes is octahedral and has not changed from that of $Ni(acac)_2$.

The magnetic and electronic data for cobalt acetylacetonate $Co(acac)_2$ and its bimetallic complexes is presented in Table III. $Co(acac)_2$ is a tetramer with a magnetic moment of 4.93 B.M. [32–35]. The complex exhibits a band in the region 18,000–22,000 cm^{-1} which has been assigned to the $^4T_{1g}(F) \to {}^4T_{1g}(P)$ transition in an octahedral field. The band has been split by reduction of symmetry and by spin–orbit coupling [36].

TABLE III. Analytical and Physical Data for Cobalt(II) Acetylacetonate and its Bimetallic Complexes.

Empirical formula of complex	%Co[a]	%Cl	%M[b]	Molar cond. (ohm^{-1} cm^2 mol^{-1})	Magnetic moment (B.M.)	Electronic transition (cm^{-1})
$(C_{10}H_{14}O_4)Co$	22.79 (22.96)			40.00	4.95	16,200
$(C_{10}H_{14}O_4)Co \cdot SiCl_4$	13.72 (13.82)	33.33 (33.26)	6.42 (6.56)	45.00	5.03	17,100
$(C_{10}H_{14}O_4)Co \cdot SnCl_4$	11.48 (11.39)	27.38 (27.41)	22.74 (22.97)	36.15	5.17	16,900
$(C_{10}H_{14}O_4)Co \cdot SeCl_4$	12.21 (12.34)	29.65 (29.71)	16.45 (16.53)	35.00	5.33	16,975
$(C_{10}H_{14}O_4)Co \cdot TeCl_4$	11.32 (11.20)	26.74 (26.94)	24.31 (24.29)	30.13	5.28	17,110

[a] Values in the parentheses are the calculated values. [b] M = Si, Sn, Se or Te.

The binuclear complexes have magnetic moments in the range 5.0 to 5.3 B.M. which is consistent with octahedral symmetry [37].

The electronic spectra of the binuclear complexes exhibit a multiple band at 17,000 cm^{-1}. The band is assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition in admixture with the weak two-electron transition, $^4T_{1g} \rightarrow {}^4A_{2g}$. The electronic and magnetic data indicate that the cobalt in the bimetallic complexes remains in an octahedral environment.

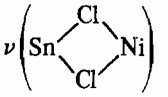
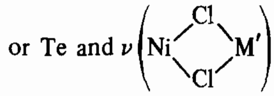
Infrared Spectra

The important IR frequencies and their assignments for the bis(acetylacetonate) metal complexes and their binuclear adducts with silicon, tin, sellenium or tellurium are available upon request from the author for correspondence.

$Cu(acac)_2$ has bands at 1575 and 1505 cm^{-1} which can be attributed to ν(C⋯O) and ν(C⋯C) stretches respectively [38, 39]. Two other important bands observed at 1275 cm^{-1} and 455 cm^{-1} are assigned to ν(C–O) and ν(Cu–O).

In the spectra of the binuclear adducts, a wide band observed at 1550 cm^{-1} can be assigned to ν(C⋯O) [40]. For the silicon adduct, the bands observed at 830 and 460 cm^{-1} have been assigned to ν(Si–O) and ν(Cu–O); whereas the four bands seen in the region 640 to 545 cm^{-1} are attributed to ν(Si–Cl) [41]. For the tin adduct, the bands observed at 460 cm^{-1} and 330 cm^{-1} are assigned to ν(Sn–O) and ν(Sn–Cl) respectively [42]. The selenium adduct has an IR spectrum with bands at 440 and 330 cm^{-1} which are assigned to ν(Se–O) and ν(Se–Cl) [43]. Similarly for the tellurium adduct, the bands for ν(Te–O) and ν(Te–Cl) are observed at 450 cm^{-1} and 345 cm^{-1} respectively [44–46].

In the spectra of $Ni(acac)_2$ the bands observed at 1580 cm^{-1} and 1530 cm^{-1} are attributed to ν(C⋯O) and ν(C⋯C) respectively [47, 48]; a strong band at 435 cm^{-1} is assigned to ν(Ni–O).

In the spectra of the binuclear adducts of $Ni(acac)_2$ the silicon adduct has a strong peak at 580 cm^{-1} attributed to ν(Si–Cl) [41], and a peak in the far-infrared region around 290 cm^{-1}; the latter absorption has been assigned to a vibration resulting from bridging chlorines bonded to nickel and silicon. In the tin adduct the bands due to ν(Sn–Cl) and  are observed at 340 and 305 cm^{-1}, respectively. Tin retains its tetrahedral environment [49]. For the selenium and tellurium adducts, the bands due to ν(Se–Cl) and ν(Te–Cl) are observed at 330 and 335 cm^{-1} respectively. It is thus apparent that the presence of bands due to ν(Ni–O), ν(M–Cl) where M = Si, Sn, Se or Te and  where M′ = Si, Sn strongly supports the interpretation that two chlorine atoms of the tetravalent metal chlorides are shared with the nickel atom, thus maintaining octahedral coordination around the nickel.

In the spectrum of $Co(acac)_2$, peaks around 1600 and 1520 cm^{-1} are assigned to ν(C⋯O) and ν(C⋯C) respectively [34]. The band around 1250 cm^{-1} is assigned to ν(C–O), while another band at 435 cm^{-1} is attributed to ν(Co–O).

In the spectra of the binuclear $Co(acac)_2$ adducts, ν(C–O) appears at 1610 cm^{-1} and ν(Co–O) appears at 450 cm^{-1}. For the silicon, tin, selenium and tellurium adducts, bands are observed at 540, 340, 330 and 335 cm^{-1} respectively. These bands are assigned to ν(Si–Cl), ν(Sn–Cl), ν(Se–Cl) and ν(Te–Cl), respectively.

A band at 300 cm^{-1} observed in the far infrared for all the complexes suggests the possibility of a chlorine bridging between cobalt and the Si, Sn, Se or Te atoms.

Biological Tests of the Complexes

(a) Evaluation of Antibacterial Activity

The degree of antibacterial activity exhibited by $Ni(acac)_2$, $Cu(acac)_2$ and $Co(acac)_2$ and their bimetallic complexes is reported in Table IV. The data have been presented in the following manner:

Diameter of zone of inhibition (mm)	Symbol	Comments
12–15	+	Insignificant activity
16–20	++	Minimum activity
21–25	+++	Moderate activity
26–35	++++	Maximum activity

It is evident from Table IV that the bimetallic complexes of $Cu(acac)_2$ and $Co(acac)_2$ with silicon, tin, selenium and tellurium exhibit moderate activity against *S. aureus*. The most promising compound is the tellurium complex of $Co(acac)_2$ which exhibits substantial activity against *B. subtilis*, *S. aureus* and *E. coli*.

(b) Acute Toxicity Studies

The results indicate that $Cu(acac)_2 \cdot SiCl_4$ and $Cu(acac)_2 \cdot SeCl_4$ have LD-50 values between 20 and 50 mg of complex per kg of body weight. The lethal dosage (concentration of complex at which all the animals die) is 100 mg of $Cu(acac)_2 \cdot SiCl_4$ per kg of bodyweight; all animals are dead within 6 hours. The lethal dosage for $Cu(acac)_2 \cdot SeCl_4$ is 50 mg of complex per kg of body weight; all animals are dead within 12 hours.

(c) Antialgal Activity Studies

The effects of acetylacetone, $Co(acac)_2$, and $Co(acac)_2 \cdot SiCl_4$ on the growth of *H. welwitschii* have been recorded in Table V. All three species inhibit the algae growth, and inhibition increases with the concentration of the compounds. $Co(acac)_2$ appears to have the greatest inhibitory effect; *H. welwitschii* dies after 20 days of exposure.

Conclusions

Based on the chemical data, the following structures are proposed for the complexes under study.

TABLE IV. Antibacterial Activity of Acetylacetone and its Complexes.

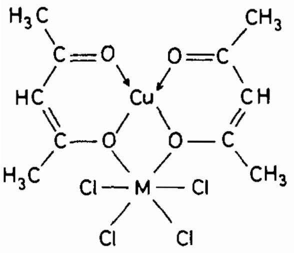
Ligand/complex	*B. subtilis* (gram positive)			*S. aureus* (gram positive)			*E. coli* (gram negative)			*P. vulgaris* (gram negative)		
	A*[a]	B*[a]	C*[a]	A	B	C	A	B	C	A	B	C
Acetylacetone	+	+	+	++	++	++	+	+	+	+	+	+
$Ni(acac)_2$	+	+	+	+	+	+	+	+	+	+	++	++
$[Ni(acac)_2] \cdot SiCl_4$	+	+	+	+	+	+	+	++	++	+	++	++
$[Ni(acac)_2] \cdot SnCl_4$	+	+	+	+	+	+	+	+	+	+	+	+
$[Ni(acac)_2] \cdot SeCl_4$	+	+	+	+	+	++	+	+	++	+	+	+++
$[Ni(acac)_2] \cdot TeCl_4$	+	+	+	+	+	++	+	++	++	+	+	+
$Cu(acac)_2$	+	++	+++	+	+	+	+	+	+	++	++	+++
$[Cu(acac)_2] \cdot SiCl_4$	++	++	+++	+++	++++	++++	+	++	++	+	+	++
$[Cu(acac)_2] \cdot SnCl_4$	++	++	+++	+++	+++	++++	+	+	+	++	++	++
$[Cu(acac)_2] \cdot SeCl_4$	++	+++	++++	+++	+++	++++	+	+	+	+	+	+
$[Cu(acac)_2] \cdot TeCl_4$	+	+++	+++	+++	++++	++++	++	++	++++	++	++	++
$Co(acac)_2$	+	++	+++	++	+++	++++	++	++	++	+	++	+++
$[Co(acac)_2] \cdot SiCl_4$	+	++	+++	+++	+++	+++	+	++	++	++	++	+++
$[Co(acac)_2] \cdot SnCl_4$	+	+	+	++	+++	+++	++	++	+++	+	++	+++
$[Co(acac)_2] \cdot SeCl_4$	+	++	+++	+++	+++	++++	+	+	+	+++	+++	+++
$[Co(acac)_2] \cdot TeCl_4$	+++	+++	+++	++++	++++	++++	++++	++++	++++	+	++	+++
DMF (solvent control)	+	+	+	+	+	+	+	+	+	+	+	+
5% phenol in water (positive control)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++

[a] A* = 50 μg/ml; B* = 100 μg/ml; and C* = 200 μg/ml.

TABLE V. Effect of Acetylacetone and its Complexes on the Growth of *H. welwitschii*.

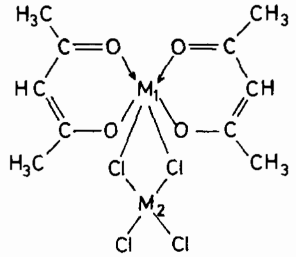
Concentration in μg/ml	Acetylacetone			$Co(acac)_2$			$Co(acac)_2SiCl_4$		
	10th day	20th day	30th day	10th day	20th day	30th day	10th day	20th day	30th day
Control	0.0199[a]	0.0301	0.0440	0.0199	0.0301	0.0440	0.0199	0.0301	0.0440
100	0.0174	0.0210	0.0274	0.0154	0.0164	0.0371	0.0070	0.0189	0.0333
200	0.0038	0.0102	0.0254	0.0098	0.0032	0.0092	0.0090	0.0175	0.0307
300	0.0030	0.0015	0.0023	0.0084	0.0000	0.0000	0.0019	0.0012	0.0069

[a] Weight (grams) of algae/10 ml.



(I)

(M = Si, Sn, Se or Te)



(II)

M_1 = Co, Ni

M_2 = Si, Sn, Se or Te

In structure II, the tetravalent metal chloride has not induced any pronounced stereochemical change in the environment of cobalt(II) or nickel(II).

The biological data indicate that the bimetallic complexes of $Cu(acac)_2$ exhibit bacterial and mammalian toxicity; whereas the $Co(acac)_2$ bimetallic complexes exhibit antibacterial and antifungal properties.

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References

1 H. F. Holtzelaw, Jr., J. P. Collman and R. M. Alire, *J. Am. Chem. Soc.*, *80*, 1100 (1958).
2 R. C. Fay, *Ann. N.Y., Acad. Sci.*, *159* (pt-1), 152 (1969).
3 J. P. Collman, R. L. Marshall, W. L. Young, III and S. D. Goldby, *Inorg. Chem.*, *1*, 704 (1962).
4 R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, *84*, 2303 (1962).
5 W. H. Nelson, *Inorg. Chem.*, *6*, 1509 (1967).
6 M. M. Crystal, *J. Econ. Entomol.*, *63*, 321 (1970).
7 C. C. Hinckley, *J. Am. Chem. Soc.*, *91*, 5160 (1969).
8 F. A. Cotton, F. A. Hart and G. P. Moss, *J. Chem. Soc. (Dalton)*, 221 (1975).
9 W. Mertz, *Physiol. Rev.*, *49*, 163 (1969).
10 W. D. Ross and R. E. Sievers, *Talanta*, *15*, 87 (1968).
11 F. P. Dwyer, E. C. Gyarfas, W. B. Rogers and J. H. Koch, *Nature*, *170*, 190 (1952).
12 G. Gillessen and E. V. Wasielewski, *Arzneim-Forschung*, *12*, 196 (1962).
13 W. K. Easley, M. B. Purvis and T. P. Copeland, *Proc. La. Acad. Sci.*, *30*, 16 (1967).
14 G. Bringmann and R. Kucha, *Mitt. Int. Ver. Theor. Angew Limnol.*, *21*, 275 (1978).
15 J. P. Fackler, Jr., *Prog. Inorg. Chem.*, *7*, 361 (1966) and references therein.
16 A. I. Vogel, 'Quantitative Inorganic Analysis', 3rd. Edition, Longmans Green & Co., London and New York (1969).
17 R. Cruickshank, 'Medical Microbiology', Eds. Churchill and Livingstone, U.K., (1965).
18 W. G. Smith, 'Progress in Medicinal Chemistry', Vol. I Ed. G. P. Ellis and G. B. West, Buttersworth, London, 1961.
19 S. G. Bharati and U. D. Bongale, *Phykos*, *15* (122), 31 (1976).
20 B. D. Sinha and H. D. Kumar, *Ann. Bot.*, *37*, 673 (1973).
21 P. Ray and D. N. Sen, *J. Ind. Chem. Soc.*, *25*, 473 (1948).
22 D. Hall, A. J. McKinnon and T. N. Waters, *J. Chem. Soc. (A)*, 615 (1966).
23 Z. A. Starikova and E. A. Shugam, *Zh. Strukt. Khim.*, *10*, 290 (1969).
24 I. Robertson and M. R. Truter, *J. Chem. Soc. A*, 309 (1967).
25 J. Denugnck, A. Viellard and Wahlgren, *J. Am. Chem. Soc.*, *95*, 5563 (1973).
26 D. W. Smith, *J. Chem. Soc. (A)*, 2900 (1970).
27 S. K. Tiwari, S. Jain, A. Kumar and K. C. Tiwari, *J. Inc. Chem. Soc.*, *57*, 571 (1980).
28 K. Akabori, H. Matsuo and Y. Yamamoto, *J. Inorg. Nucl. Chem.*, *33*, 2593 (1971).

29 F. K. C. Lyle, B. Morosin and E. C. Lingafelter, *Acta Cryst.*, *12*, 938 (1959).
30 C. K. Jorgensen, *Acta Chem. Scand.*, 9, 1362 (1955).
31 O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, *26*, 1686 (1957).
32 F. A. Cotton and R. C. Elder, *Inorg. Chem.*, *4*, 1145 (1965).
33 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 3rd. Ed., Interscience Publishers (1972).
34 R. H. Holm and M. J. O'Connor, 'Progress in Inorganic Chemistry', Vol. 14, Ed., S. J. Lippard, Wiley Interscience (1971).
35 C. J. Ballhausen, 'Introduction to Ligand Field Theory', McGraw Hill, New York, N.Y., (1962).
36 F. A. Cotton and R. C. Elder, *J. Am. Chem. Soc.*, *86*, 2294 (1964).
37 M. Calvin and C. H. Barkelew, *J. Am. Chem. Soc.*, *68*, 2267 (1946).
38 L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4491 (1954).
39 J. Lecomte, *Discuss. Farad. Soc.*, 9, 125 (1950).
40 C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, *30*, 2723 (1968).
41 A. L. Smith, *Spectrochim. Acta*, *19*, 849 (1963).
42 N. S. Biradar, B. R. Patil and V. H. Kulkarni, *J. Inorg. Nucl. Chem.*, *37*, 1901 (1975).
43 W. E. Rudzinski, T. M. Aminabhavi, N. S. Biradar and C. S. Patil, *Inorg. Chim. Acta*, *67*, 177 (1982).
44 K. Nakamoto, 'Spectroscopy and Structure of Metal Chelate Compounds', Eds. K. Nakamoto and P. J. McCarthy, Wiley-Interscience, New York (1968).
45 W. R. McWhinnie and P. Thavornyutikarn, *J. Chem. Soc., Dalton*, 516 (1972).
46 E. R. Clark, A. J. Collect and D. G. Naik, *J. Chem. Soc., Dalton*, 1961 (1973).
47 K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, *J. Am. Chem. Soc.*, *83*, 1066 (1961).
48 B. P. Susz and I. Cooke, *Helv. Chim. Acta*, *37*, 1273 (1954).
49 R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, *4*, 350 (1965).