

TABLE 1 — ANALYSES, MELTING POINTS, MAGNETIC MOMENTS AND ELECTRONIC SPECTRAL DATA OF SOME ANIONIC COBALT (II) COMPLEXES

Compound	m.p. (°C)	Found (Calc.), %			μ_{eff} (B. M.)	ν_{max} (ϵ) (cm^{-1})
		Co	Cl	Br		
[QH] [CoCl ₂ BrQ]	216	12.48 (12.57)	15.10 (15.13)	17.02 (17.05)	4.57	16180 (131), 15270 (109), 14920 (48)
[QH] [CoCl ₃ Q]	205	13.71 (13.89)	24.96 (25.05)	—	4.54	16350 (175), 15700 (91), 15050 (35)
[QH] [CoBr ₃ Q]	232	10.50 (10.57)	—	42.85 (43.00)	4.56	16260 (186), 15380 (261), 15050 (101)
[QH] [CoBr ₂ ClQ]	208	11.24 (11.48)	6.85 (6.90)	31.00 (31.14)	4.40	16580 (269), 15160 (161), 14920 (168)
[IQH] [CoCl ₂ BrIQ]	188	12.50 (12.57)	15.08 (15.13)	16.98 (17.05)	4.58	16280 (163), 15270 (142), 14880 (89)
[IQH] [CoCl ₃ IQ]	190	13.80 (13.89)	25.00 (25.05)	—	4.63	16340 (144), 15340 (105), 15050 (57)
[IQH] [CoBr ₃ IQ]	203	10.48 (10.57)	—	42.70 (43.00)	4.67	16260 (240), 15500 (130), 15020 (70)
[IQH] [CoBr ₂ Cl IQ]	185	11.44 (11.48)	6.88 (6.90)	31.02 (31.14)	4.46	16130 (221), 15270 (194), 14970 (124)

only two halogen atoms instead of three shown in the present investigation, since the ring halogen can not be liberated by the treatment of dilute nitric acid and requires prior fusion. Moreover, the product would have been a non-electrolyte whereas all the compounds reported here are 1:1 electrolytes, Λ_M being in the range of 90–150 mho $\text{cm}^2 \text{mole}^{-1}$. Hence, it is assumed that the halogen reacts with hydrogen of ethanol forming the corresponding hydrogen halide which forms quaternary halides with nitrogen donor ligands giving rise to tetra coordinated anionic complexes containing a ligand molecule bonded to metal ion.

The infrared spectra of these compounds were recorded using hexachlorobutadiene as mulling agent and the $\nu\text{N-H}$ and $\delta\text{N-H}$ frequencies were observed around 3000–3500 and $\sim 1500 \text{ cm}^{-1}$ respectively. The presence of these N–H absorption bands is a definite indication of the presence of quinolinium and isoquinolinium cations in the complexes.

All the complexes exhibit intense bands in the region 14,880–16,580 cm^{-1} in their solution electronic spectra (Table 1) characteristic of cobalt(II) ion in a tetrahedral environment. The band near 16000 cm^{-1} is associated with the transition $4A_2(F) \rightarrow 4T_1(P)$ for a species of undistorted tetrahedral symmetry. The complexity of the bands in this region is attributed to spin-orbit coupling effect which splits the $4T_1(P)$ state and allows the transition to the neighbouring doublet state to gain some intensity. Molar extinction coefficients (ϵ) for tetrahedral complexes are high compared to octahedral complexes and the values of ϵ for the complexes under report lie within the range reported for tetrahedral cobalt(II) complexes in the literature¹⁴.

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References

1. ROY, P. C. & RAO, D. V. R., *Indian J. Chem.*, **9** (1971), 1146.
2. KING, H. C. A., KORES, E. & NELSON, S. M., *J. chem. Soc.*, (1963), 5449.

3. KING, H. C. A., KORES, E. & NELSON, S. M., *J. chem. Soc.*, (1964), 4832.
4. NYHOLM, R. S., *Chem. Rev.*, **53** (1953), 263.
5. NYHOLM, R. S., *Q. Rev. chem. Soc. London*, **7** (1953), 377.
6. BABAeva, A. V., BARANOVSKII, I. V. & AFANASEVA, G. G., *Zh. neorg. Khim.*, **10** (1965), 1268.
7. SAHA, C. & SEN, DEBABRATA, *Proc. of 56th Indian Science Congress Association. Part III*, 1969, 96.
8. BABAeva, A. V. & BARANOVSKII, I. V., *Russ. J. inorg. Chem.*, **4** (1959), 343.
9. MISRA, M. K. & RAO, D. V. R., *J. organometal. Chem.*, **22** (1970), 227.
10. DAS, A. K. & RAO, D. V. R., *Z. anorg. allg. Chem.*, **379** (1970), 213.
11. MAGUIRE, K. D. & JONES, M. M., *J. Am. chem. Soc.*, **84** (1962), 2316.
12. NELSON, JANE & NELSON, S. M., *J. chem. Soc.*, (1969), 1597.
13. FIGGIS, B. M. & NYHOLM, R. S., *J. chem. Soc.*, (1954), 12; (1959), 338.
14. BRIGGS, E. M. & HILL, A. E., *J. chem. Soc.*, (1969), 1835.

Synthesis, Magnetic & Spectral Studies On Some Adducts of Manganese(II) Acetylacetonate

D. S. SANKHLA, R. C. MATHUR† & SUDHINDRA N. MISRA*

Department of Chemistry, University of Jodhpur
JodhpurReceived 14 February 1979; revised 26 July 1979; accepted
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Adducts of manganese(II) acetylacetonate with sulphur and nitrogen containing ligands have been prepared. Their diffuse reflectance spectra, infrared spectra and magnetic properties have been investigated. Racah inter-electronic repulsion parameter B and C , Slater-Condon-Shortley parameter F_2 and F_4 , crystal field splitting energy (Dq), nephelauxetic ratio and ligand contribution to complex (h_x) have been calculated. It has been possible to distinguish between the sulphur and nitrogen coordination of thioureas on the basis of IR data.

†Physics Division, Defence Laboratory, Jodhpur.

MANGANESE(II) ion having a d^5 configuration generally forms high-spin complexes, because of the additional stability of the half filled d -shell. The equilibrium constants for their formation in aqueous solution are not high as compared to those for bivalent cations of succeeding element (Fe^{2+} - Cu^{2+}), because manganese(II) is the largest of these and no ligand field stabilization energy is operative in its complexes¹. Manganese(II) complexes are susceptible to oxidation², but the complexes synthesized in the present study have been found to be sufficiently stable and resist oxidation. We report here the syntheses and magnetic and spectral properties of the adducts of diaquobis-(acetylacetonato) manganese (II) with thiourea(Tu), phenylthiourea (PhTu), benzoylthiourea (BenzTu), thiosemicarbazide (Tsc), pyridine(Py), 1,10-phenanthroline(Phen), α,α' -dipyridyl (Dipy) and 8-hydroxyquinoline (8-HQu).

Chemicals used were of AR grade. Ethanol was distilled over magnesium ethoxide prepared from magnesium and ethanol in the presence of iodine.

Preparation of adducts — The adducts were prepared through ligand-exchange reactions of diaquobis (acetylacetonato) manganese (II). An ethanolic solution of the parent complex diaquobis-(acetylacetonato)manganese(II)³ (0.01 mol) and the ligand (0.02 mol for unidentate ligand and 0.01 mol for bidentate ligand) were refluxed under nitrogen atmosphere. On cooling, the complex separated out from the solution and was filtered, washed with ethanol-ether and dried *in vacuo* over anhydrous calcium chloride. The purity of these complexes was established on the basis of elemental analyses (Table 1).

Magnetic measurements were carried out on a Gouy magnetic balance at $300 \pm 1^\circ\text{K}$. Diffuse reflectance spectra in the UV-visible region were measured on a Carl Zeiss Jena VSU-2P spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer model- 577 in KBr phase.

Since high-spin Mn(II) complexes have an orbitally non-degenerate ^6S ground term, the spin-only magnetic moment of 5.92 B. M. is expected which will be independent of the temperature and of the stereochemistry⁴⁻⁶. The present complexes show magnetic moment values in the range 5.87-6.08 B. M. indicating the presence of five unpaired electrons and hence these are high spin complexes.

The IR spectrum of the parent complex shows the presence of coordinated water molecules as revealed by a band at 3360 cm^{-1} , whereas, the adducts derived from it do not show absorption in this region, indicating the replacement of the water molecules by the reacting ligands. The significant strong absorptions due to coordinated acetylacetonate are $\nu(\text{C}-\text{O})$ and $\nu(\text{C}-\text{C})$, and these have been observed in the region $1590-1610$ and $1495-1512\text{ cm}^{-1}$ respectively, while the absorption due to $\nu(\text{M}-\text{O})$ has been observed in the region $400-415\text{ cm}^{-1}$.

The high frequency -NH absorption bands of thiourea shift to higher frequency region on complexation indicating thereby that the coordination of thiourea ligands to the metal ion is through S-atom^{8,9}. A strong band at 805 cm^{-1} in thiosemicarbazide is due to $\text{C}=\text{S}$ stretching with some contribution from NH_2 deformation or NCN stretching. This band also gets shifted to the lower frequency region (698 cm^{-1}) in the adduct, supporting our contention that the coordination of ligand is through S-atom^{10,11}. A moderately intense band occurring around 1610 cm^{-1} region in the S-containing adducts has been assigned to $-\text{NH}_2$ deformation.

The strong bands observed at 1595 and 635 cm^{-1} in the pyridine adduct attributed to $8a$ (Py-ring deformation) and $6a$ (in-plane ring deformation) modes respectively, correspond to 1585 and 600 cm^{-1} bands of pyridine. This upward shift indicates the N-coordination of the ligand to the metal ion^{12,13}. The skeletal vibration of pyridine (1020 cm^{-1}) also gets shifted to higher frequency region (1060 cm^{-1}) on complexation. The strong absorptions occurring at 1430 and 1380 cm^{-1} in the phenanthroline adduct have been assigned to $\nu\text{C}=\text{C}$ and $\nu\text{C}=\text{N}$ vibrations respectively¹⁴. The $\nu\text{C}=\text{N}$ vibrations in the dipyridyl adduct have been observed in the region $1470-1580\text{ cm}^{-1}$ while the strong vibrations discernible at 765 and 670 cm^{-1} in the adduct have been attributed to out-of-plane bending of the ring hydrogen atoms¹⁵. A moderately intense band occurring at 3520 cm^{-1} in the 8-hydroxyquinoline adduct has been assigned to O-H vibration. The absorption due to $\nu\text{C}=\text{N}$ and $\nu\text{C}=\text{O}$ vibrations¹⁶ occurring at 1595 and 1090 cm^{-1} in 8-HQu ligand have been observed at 1610 and 1105 cm^{-1} respectively in the 8-HQu adduct.

In Mn(II) complexes the intensity of the electronic transitions from the ground state (^6S) to the states of four-fold multiplicity are very weak and since Mn(II) has a d^5 electronic configuration the same type of energy-level diagram applies whether the metal ion is surrounded by tetrahedral or octahedral environment. The spectra in the solution could not be obtained because of the weak intensity of the bands and lack of the high solubility of these complexes in organic

TABLE 1—ANALYTICAL AND MAGNETIC MOMENT DATA OF THE COMPLEXES

Complex	Found (Calc.), %			μ_{eff} (B.M.)
	M	N	S	
$\text{Mn}(\text{AcAc})_2(\text{H}_2\text{O})_2$	(18.99) 18.9	—	—	6.01
$\text{Mn}(\text{AcAc})_2(\text{Tu})_2$	(13.55) 13.4	(13.82) 13.7	(15.81) 15.7	6.08
$\text{Mn}(\text{AcAc})_2(\text{PhTu})_2$	(9.85) 9.8	(10.04) 10.1	(11.50) 11.4	6.06
$\text{Mn}(\text{AcAc})_2(\text{BenzTu})_2$	(8.96) 8.9	(9.13) 9.1	(10.45) 10.4	5.94
$\text{Mn}(\text{AcAc})_2(\text{Tsc})_2$	(12.61) 12.5	(19.3) 19.2	(14.72) 14.7	5.98
$\text{Mn}(\text{AcAc})_2(\text{Py})_2$	(13.35) 13.4	(6.81) 6.8	—	5.90
$\text{Mn}(\text{AcAc})_2(\text{Phen})$	(12.67) 12.6	(6.46) 6.5	—	5.88
$\text{Mn}(\text{AcAc})_2(\text{Dipy})$	(13.42) 13.4	(6.84) 6.8	—	5.88
$\text{Mn}(\text{AcAc})_2(8\text{-HQu})$	(13.79) 13.8	(3.51) 3.4	—	5.87

TABLE 2 — EXPERIMENTAL TRANSITION ENERGIES AND CALCULATED VALUES FOR PARAMETERS B , C , Dq , F_2, F_4 (in cm^{-1}), β AND h_x

Complex	${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4P)$	${}^6A_{1g} \rightarrow {}^4E_g({}^4D)$	${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}({}^4G)$	${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$	B	C	Dq	F_2	F_4	β	h_x
Mn(AcAc) ₂ (H ₂ O) ₂	32786	28571	24875	20000	528.0	3919.0	850	1088.0	111.9	0.67	4.71
Mn(AcAc) ₂ (Tu) ₂	32573	26666	23529	20325	448.1	3809.5	800	992.1	108.8	0.57	6.14
Mn(AcAc) ₂ (PhTu) ₂	32786	27932	24691	19920	463.0	4012.2	856	1036.0	114.6	0.58	5.87
Mn(AcAc) ₂ (BenzTu) ₂	32154	27548	23980	19646	509.7	3776.5	888	1049.2	107.9	0.64	5.02
Mn(AcAc) ₂ (Tsc) ₂	32258	27397	23809	19685	512.5	3736.6	882	1046.0	106.7	0.65	4.97
Mn(AcAc) ₂ (Py) ₂	32258	27624	24691	20202	419.0	3913.0	815	978.0	111.8	0.53	6.67
Mn(AcAc) ₂ (Phen)	33333	27777	24390	20202	483.8	3910.3	815	1042.3	111.7	0.61	5.49
Mn(AcAc) ₂ (Dpiy)	35714	27247	24390	19801	408.1	4061.7	873	988.1	116.0	0.51	6.86
Mn(AcAc) ₂ (8-HQu)	33333	28409	25000	19607	487.0	4026.0	895	1062.0	115.0	0.62	5.42

solvents. Hence diffuse reflectance spectra have been recorded. Out of the six electronic spectral bands of the hexaquo manganese(II) ion, only four bands could be observed in the diffuse reflectance spectra of these complexes. The observed bands representing corresponding transitions and energies in terms of Racah parameter¹⁷ are: ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$, $(10B + 5C)$; ${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}({}^4G)$, $(10B + 5C)$; ${}^6A_{1g} \rightarrow {}^4E_g({}^4D)$, $(17B + 5C)$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4P)$, $(7B + 7C)$. The electronic spectral patterns of all the complexes have been found to be similar. The energies of ${}^6A_{1g} \rightarrow {}^4E_g({}^4D)$ and ${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}({}^4G)$ transitions are independent of Dq and depend^{18,19} only on B and C , and hence these have been used to calculate the values for parameter B and C . The value for the parameter Dq could be evaluated using the transition ${}^6A_{1g} \rightarrow {}^4E_g({}^4G)$ with the help of the plot of transition energies vs Dq given by Orgel²⁰. The values for Slater-Condon-Shortley²¹ parameter F_2 and F_4 , nephelauxetic ratio (β) and nephelauxetic parameter for coordinated ligands²² (h_x) have been calculated. The observed transition energies and calculated parameters are given in the Table 2. It has been observed that the lower value of β and higher value of h_x for the adducts as compared to the parent complex indicate the increase in covalent character.

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References

1. COTTON, F. A. & WILKINSON, G., *Advanced inorganic chemistry* (John Wiley, Eastern, New Delhi), 1967, 836.
2. BOUCHER, L. J. & COE, C. G., *Inorg. Chem.*, **14** (1975), 1289.
3. CHARLES, G., *Inorganic synthesis* (McGraw Hill, Inc., New York), **6** (1960), 164.
4. COLLINE, R. J. & LARKWORTH, L. F., *J. inorg. nucl. Chem.*, **37** (1975), 334.
5. FIGGIS, B. N. & LEWIS, J., *Prog. inorg. Chem.*, **6** (1964), 102.
6. SHIMAN, O. & GRAY, H. B., *Inorg. Chem.*, **13** (1974), 1185.
7. NAKAMOTO, K., *Infrared & raman spectra of inorganic and coordination compounds* (John Wiley, New York), 1978, 249.

8. YAMAGUCHI, A., PENLAND, R. B., MIZUSHIMA, S., LANE, T. J., COLUMBA, C. & QUAGLIANO, J. V., *J. Am. chem. Soc.*, **80** (1958), 527.
9. BAILEY, R. A. & PEARSON, T. R., *Can. J. Chem.*, **46** (1968), 3119.
10. WILES, D. M. & SUPERUNCHUK, *Can. J. Chem.*, **47** (1969), 1087.
11. BEECROFT, B., CAMBELL, M. J. M. & GRZESKOWIAK, R., *J. inorg. nucl. Chem.*, **36** (1974), 55.
12. GILL, N. S., NUTALL, R. H., SCAIFE, D. E. & SHARP, D. W. A., *J. inorg. nucl. Chem.*, **18** (1961), 79.
13. ROBIN, J. H., CLARK & WILLIAMS, C. S., *Inorg. Chem.*, **4** (1965), 350.
14. SCHILT, A. A. & TAYLOR, R. C., *J. inorg. nucl. Chem.*, **9** (1959), 211.
15. SINHA, S. P., *Indian J. Chem.*, **8** (1970), 82.
16. VASIREDDI, S. P. & RAMACHANDRA RAO, V., *J. inorg. nucl. Chem.*, **39** (1977), 311.
17. HEIDT, L. J., KOSTER, G. F. & JOHNSON, A. M., *J. Am. chem. Soc.*, **80** (1958), 6471.
18. OLAVI, S. & HARRY, B. G., *Inorg. Chem.*, **13** (1974), 1185.
19. PRETI, C. & TOSI, G., *Aust. J. Chem.*, **29** (1976), 543.
20. ORGEL, L. E., *J. chem. phys.*, **23** (1955), 1004.
21. HUHEEY, J. E., *Principles of structure & reactivity* (Harper & Row, New York), 1972, 363.
22. JORGENSON, C. K., *Oxidation number & oxidation states* (Springer, New York), 1969, 106.

Magnetic & Spectroscopic Behaviour of Some Copper(II) Oxalate Complexes

P. C. SRIVASTAVA*, S. BANERJEE & B. K. BANERJEE
Research & Development, The Fertilizer (P & D) India Ltd.,
P.O. Sindri 828 122

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The magnetic susceptibility, electronic and ESR spectral data of a series of copper(II) oxalate complexes with ammonia, methyl amine, ethylenediamine, aniline and pyridine are reported. All the complexes except Cu(oxalate)(ethylenediamine)₂, which has a tetragonally distorted octahedral structure, have been assigned nearly square-planar structures.

COMPLEXES of copper(II) with oxalic acid and different amines have been the subject of intensive studies¹⁻⁴. In the present work, electronic and ESR spectra, and magnetic susceptibility measurements are reported on some copper(II) oxalate complexes with ammonia, methyl amine, ethyl amine,