

Mixed ligand complexes of *bis*(acetylacetonato) nickel(II) and cobalt(II) with N and N,N'-substituted thioureas

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Abstract. Several mixed ligand complexes of nickel(II) and cobalt(II) acetylacetonates with N-substituted thioureas such as ortho, meta and para chlorophenyl, parabromophenyl and orthotolyl thioureas and N,N'-substituted thioureas such as N-benzoyl N'-ethyl thiourea, N-benzoyl N'-phenyl thiourea, N-benzoyl N'-o-chlorophenyl thiourea, N-benzoyl N'-o-tolyl thiourea, N-benzoyl N'-o-methoxyphenyl thiourea, N-benzoyl N'-cyclohexyl thiourea, N-benzoyl N'-2,5 dimethoxyphenyl thiourea, N-benzoyl N'-2,5 diethoxyphenyl thiourea, N-benzoyl N'- β -hydroxyethyl thiourea, N-benzoyl N'-furfuryl thiourea, N-benzoyl N'-orthohydroxyphenyl thiourea and N-phenyl N'-orthomethoxyphenyl thiourea, have been synthesized and characterized on the basis of elemental analysis, conductivity, molecular weight determination and magnetic moments. The nature of the bonding and the structure of the complexes have been proposed from the infrared and electronic spectral studies.

Keywords. Mixed ligand complex; acetylacetonates; nickel(II) and cobalt(II) thioureas; magnetic spectra.

1. Introduction

Although a considerable amount of work has been done on the complexes of metal β -diketones such as *bis*(acetylacetonato) nickel(II) with nitrogen and oxygen donor ligands (Misra and Ramanrao 1969; Graddon 1969; Syamal 1968), very few reports are available on the analogous sulphur-containing complexes (Misra and Ramanrao 1973). Hence, it was considered worthwhile to undertake a systematic study of the mixed complexes derived from N and N,N' substituted thioureas with nickel(II) and cobalt(II) acetylacetonates.

2. Experimental

2.1. Synthesis of ligands

The N-substituted thioureas were prepared from the appropriate amines, ammonium or potassium thiocyanate and hydrochloric acid in accordance with published procedures (Kurzer 1958). The N,N'-disubstituted thioureas were synthesized employing benzoylisothiocyanate or phenyl isothiocyanate and the corresponding amines according to the method of Douglass and Dains (1934).

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2.2 Synthesis of complexes

The nickel(II) or cobalt(II) acetylacetonate dihydrate and the ligands were mixed in ethanol in 1:2 mole ratio, refluxed for half an hour and then cooled. The complex which separated was filtered under suction, washed successively with alcohol and ether and dried in vacuum over P_2O_5 .

2.3 Analysis of complexes

The complexes were analysed for nickel (gravimetric–dimethylglyoxime), cobalt (oxinate method–gravimetric), nitrogen and sulphur by standard methods (Vogel 1962). Analysis of carbon and hydrogen has been carried out by microchemical methods.

2.4 Physico-chemical measurements

Conductivity measurements of the complexes in dimethylformamide were carried out on an Elico conductivity bridge type CM-82 with a dip type conductivity cell having cell constant 0.63. The molecular weight of a few complexes was determined by the cryoscopic method using nitrobenzene as solvent. The magnetic susceptibility of the complexes at room temperature ($\sim 26^\circ\text{C}$) was determined by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. The infrared spectra ($4000\text{--}625\text{ cm}^{-1}$) of ligands and complexes, as KBr pellets, were recorded on a Perkin-Elmer model 257 spectrometer. Infrared spectra ($200\text{--}10\text{ cm}^{-1}$) were recorded on a Polytech FIR-30 spectrometer. The electronic spectra of the complexes in the solid phase ($1500\text{--}350\text{ nm}$) were taken on a Beckmann DMR-21 spectrophotometer.

3. Results and discussion

3.1 Physical properties

The mixed ligand complexes of nickel(II) and cobalt(II) acetylacetonates with N-benzoyl N'-aryl/alkyl substituted thioureas are greenish yellow and greenish brown respectively, and they are insoluble in common organic solvents. Chemical analysis data (table 1) reveal a 1:2 ratio for metal to ligand in the complexes under present study. The molar conductance values (0.5 to $15\text{ mho cm}^2\text{ mol}^{-1}$) are too low to account for any anionic dissociation of the complexes.

3.2 Infrared spectra

The complexes exhibit intense hydrogen bonding as shown by some negative shift coupled with reduction in intensity for the νNH band ($3320\text{--}3000\text{ cm}^{-1}$).

A slight positive shift (2 to 16 cm^{-1}) for the $\nu_{\text{asym}}\text{NCN} + \delta\text{NH}_2$ band in the region $1542\text{--}1475\text{ cm}^{-1}$ and a negative shift (2 to 15 cm^{-1}) for the $\nu\text{CS} + \nu\text{CN}$ band in the region $769\text{--}701\text{ cm}^{-1}$, coupled with reduction in intensity in the case of the complexes as compared to free ligands, reveal 'S' bonding of all thioureas [Jensen and Nielsen 1966] except for N-benzoyl, N'- β -hydroxy-ethyl thiourea (N-bz N'- β (OH)etu). Further the negative shift $2\text{--}28\text{ cm}^{-1}$ for the νCS band in the region $695\text{--}650\text{ cm}^{-1}$ on com-

Table 1. Elemental analysis of complexes.

Complex number	Complex	% Ni/Co	%N	%S	%C	%H	Mol. wt.
1	Ni(acac) ₂ (bz- <i>o</i> -Clptu) ₂	7.14 (6.97)	6.81 (6.70)	7.56 (7.65)	—	—	887 (838)
2	Ni(acac) ₂ (bz-ptu) ₂	7.77 (7.68)	7.25 (7.25)	8.12 (8.32)	—	—	799 (769)
3	Ni(acac) ₂ (bz- <i>o</i> -totu) ₂	7.51 (7.36)	7.05 (6.97)	8.09 (8.03)	—	—	764 (797)
4	Ni(acac) ₂ (bz-etu) ₂	8.75 (8.72)	8.65 (8.32)	9.46 (9.52)	—	—	706 (673)
5	Ni(acac) ₂ (bz- <i>o</i> -meoptu) ₂	7.24 (7.08)	7.05 (6.75)	7.64 (7.72)	—	—	785 (829)
6	Ni(acac) ₂ (bz-cyhxtu) ₂	7.53 (7.54)	7.18 (7.17)	7.96 (8.20)	58.68 (58.39)	6.38 (6.45)	813 (781)
7	Ni(acac) ₂ (Ph- <i>o</i> -meoptu) ₂	7.57 (7.59)	7.59 (7.24)	8.27 (8.33)	58.86 (59.00)	5.62 (5.47)	723 (773)
8	Ni(acac) ₂ (bz- <i>o</i> -OHptu) ₂	7.36 (7.32)	7.01 (6.97)	8.20 (8.01)	—	—	—
9	Ni(acac) ₂ (bz-β-OHetu) ₂	8.22 (8.32)	7.80 (7.94)	8.93 (9.08)	—	—	—
10	Ni(acac) ₂ (bz-2,5 dietopty) ₂	6.17 (6.20)	5.84 (5.92)	6.66 (6.78)	—	—	903 (945)
11	Ni(acac) ₂ (bz-2,5 dimeoptu) ₂	6.57 (6.59)	6.19 (6.29)	7.10 (7.20)	—	—	899 (889)
12	Ni(acac) ₂ (bz-furfu) ₂	7.44 (7.55)	6.99 (7.20)	8.08 (8.24)	55.32 (55.61)	4.86 (4.93)	758 (777)
13	Co(acac) ₂ (<i>o</i> -Clptu) ₂	9.40 (9.39)	9.11 (8.89)	10.05 (10.17)	45.97 (45.72)	4.62 (4.48)	—
14	Co(acac) ₂ (<i>p</i> -Clptu) ₂	9.31 (9.39)	8.83 (8.89)	10.14 (10.17)	—	—	—
15	Co(acac) ₂ (<i>m</i> -Clptu) ₂	9.41 (9.39)	9.12 (8.89)	10.32 (10.17)	—	—	—
16	Co(acac) ₂ (<i>o</i> -totu) ₂	10.16 (9.84)	9.65 (9.52)	10.53 (10.87)	—	—	—
17	Co(acac) ₂ (<i>p</i> -Brptu) ₂	8.26 (8.21)	8.24 (7.79)	8.74 (8.90)	40.26 (40.07)	3.84 (3.92)	—

* Abbreviations used: acac = acetylacetonate; bz = benzoyl; Clptu = chlorophenyl thiourea; ptu = phenyl thiourea; totu = tolylthiourea; etu = ethyl thiourea; meoptu = methoxy phenyl thiourea; cyhxu = cyclohexyl thiourea; furfu = furfuryl thiourea; Brptu = bromophenyl thiourea Ph = Phenyl.

plexation followed by the appearance of a ν M-S band at $\sim 340 \text{ cm}^{-1}$ also support 'S' coordination of the ligand to the central metal ion. However, in the case of the complex derived from N-bz N'-β(OH)etu, a marked negative shift for the δNH_2 band in the 1600 cm^{-1} region and a slight positive shift with no reduction in intensity for the νCS and $\nu\text{CS} + \nu\text{CN}$ bands favour nitrogen bonding of the ligand to the central metal ion. The possibility of coordination through the 'O' of the $>\text{C}=\text{O}$ of the benzoyl group is overruled as the band around 1650 cm^{-1} remains unaffected on complexation.

The coordination of the 'O' of the $>\text{C}=\text{O}$ group of the other ligand acetylacetonate to the central metal ion is indicated by a slight positive or negative shift (5 to 10 cm^{-1}) for the C=O compared to that of diaquo nickel(II)/cobalt(II) bis acetylacetonate at

Table 2. Electronic spectral data of complexes in solid phase.

Complex number	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_2/ν_1	B'	β	ν_2 (cm^{-1}) (calcd.)	% Distortion	LFSE kcal/mole	μ_{eff} (B.M.)
1	10889	17543	30383	1.64	1017	0.977	16644	5.40	37.3	2.88
2	10889	17543	29154	1.64	935	0.899	16808	4.37	37.3	2.90
3	8333	14814	25000	1.77	987	0.949	12798	15.75	28.6	2.86
4	11235	17182	30383	1.53	924	0.888	16591	3.56	38.5	2.85
5	10630	17391	29850	1.64	1023	0.984	16591	4.82	36.4	3.07
6	10500	17220	28540	1.64	950	0.914	17070	0.87	36.0	2.85
7	10526	16528	29850	1.57	986	0.948	14558	13.53	36.0	2.80
8	9525	17699	25000	1.85	941	0.905	15332	15.43	32.6	2.86
9	10000	16666	26315	1.66	865	0.830	16076	3.67	34.3	3.42
10	8368	17391	22727	2.07	1000	0.961	14286	21.73	28.7	2.87
11	8368	16949	23392	2.02	1015	0.976	13717	23.56	28.7	2.86
12	9090	17094	26019	1.88	1056	1.010	14993	14.01	31.2	2.89
13	8333	16100	19047	1.93	889	0.916	—	—	19.04	5.03
14	8333	16129	19230	1.94	901	0.920	—	—	19.04	5.24
15	8333	16339	19531	1.96	901	0.937	—	—	19.04	5.00

Free ion values: for $\text{Ni}^{2+} = 1040 \text{ cm}^{-1}$; for $\text{Co}^{2+} = 976 \text{ cm}^{-1}$.

$\sim 1575 \text{ cm}^{-1}$. This is also supported by the shift in ν_{M-O} of parent acetylacetonates ($\sim 430 \text{ cm}^{-1}$) to lower frequencies (Calvin and Wilson 1945; Haigh *et al* 1970).

3.3 Electronic spectra

Solid state electronic spectra of the present $\text{Ni}(\text{acac})_2$ thioureas exhibit three bands at $\sim 10000 \text{ cm}^{-1}$ [${}^3T_{2g} \leftarrow {}^3A_{2g}(F), \nu_1$], $\sim 15000 \text{ cm}^{-1}$ [${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F), \nu_2$] and $\sim 29000 \text{ cm}^{-1}$ [${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F), \nu_3$]. The ligand field parameters such as Dq , ν_2/ν_1 , B' and β have been computed (Drago 1965). It is clear from the table (table 2) that the low value of ν_2/ν_1 supports the octahedral nature of these nickel(II) complexes. The percentage distortion and the extent of covalency of the metal to ligand bond are also shown in the above table.

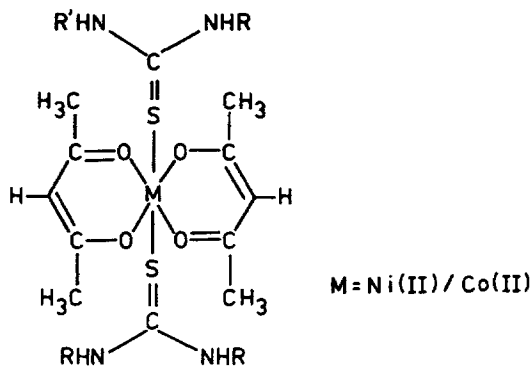
The present mixed ligand complexes of $\text{Co}(\text{acac})_2$ exhibit three low intensity bands in the regions: $\sim 8333 \text{ cm}^{-1}$ (ν_1), $\sim 16100 \text{ cm}^{-1}$ (ν_2) and 19000 cm^{-1} (ν_3), corresponding to the transitions ${}^4T_{2g} \leftarrow {}^4T_{1g}(F)$, ${}^4A_{2g} \leftarrow {}^4T_{1g}(F)$ and ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$, respectively. The ligand field parameters were calculated (Rastogi *et al* 1975) and are presented in table 2. The ligand field stabilization energy (LFSE) values for these compounds, $\sim 30 \text{ kcal/mol}$ for nickel(II) and $\sim 19 \text{ kcal/mol}$ for cobalt(II) agree fairly well with the values reported for octahedral complexes (Rastogi *et al* 1975; Eilbeck *et al* 1967) of Co(II) and Ni(II). The high B' and β values obtained here may be due to configurational interaction in the case of weak ligands such as the present thioureas (Lever 1968). However, the ν_2/ν_1 values (1.93–1.96) agree reasonably well with an octahedral stereochemistry for the present Co(II) complexes.

3.4 Magnetic susceptibility measurements

The effective magnetic moment (μ_{eff}) values at room temperature for Ni(II) and Co(II) complexes lie in the range 2.8–3.4 and 5.0–5.2 B.M. respectively. The higher μ_{eff} values compared to the spin only value of 2.8 B.M. (Ni^{2+})/3.87 (Co^{2+}) may indicate spin-orbit coupling.

4. Conclusion

On the basis of the above spectral, magnetic and analytical studies, the following tentative structure is proposed for $\text{ML}_2(\text{acac})_2$ complexes:



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References

- Calvin M and Wilson K W 1945 *J. Am. Chem. Soc.* **67** 2003
Douglass I B and Dains F B 1934 *J. Am. Chem. Soc.* **56** 1408
Drago R S 1965 *Physical methods in inorganic chemistry* (New York: Reinhold) p. 410
Eilbeck W J, Holmes F and Underhill A E 1967 *J. Chem. Soc. A* 757
Graddon D P 1969 *Coord. Chem. Rev.* **4** 19
Haigh J M, Slabbert N P and Thornton D A 1970 *J. Inorg. Nucl. Chem.* **32** 3635
Jensen K A and Nielsen P H 1966 *Acta Chem. Scand.* **20** 597
Kurzer F 1958 *Organic synthesis* (New York: John Wiley) vol. 31, p. 21
Lever A B P 1968 *Inorganic electronic spectroscopy* (New York: Elsevier) p. 187
Misra M K and Ramanrao D V 1969 *J. Inorg. Nucl. Chem.* **31** 3875
Misra M K and Ramanrao D V 1973 *J. Indian Chem. Soc.* **L** 460
Rastogi K D, Sharma K C, Dua S K and Teotia M P 1975 *J. Inorg. Nucl. Chem.* **37** 685
Syamal A 1968 *J. Inst. Chem. (India)* **40** 105
Vogel A I 1962 *Text book of quantitative inorganic analysis* (London: ELBS Longmans) pp. 256, 462 and 479