

## Synthesis and Characterization of Some Transition Metal Complexes of Dithiocarbamate Ligand Derived from *p*-Toluidine

MOHAMMAD TARIQUE and MOHAMMAD ASLAM\*

Department of Chemistry, G.F. Post Graduate College, Shahjahanpur-242 001, India

Transition metal complexes with dithiocarbamate ligand derived from *p*-toluidine and selected metal ions of 3*d*-series have been synthesized and characterized by elemental analyses, conductivity measurements and Fourier transform infrared spectroscopic technique. All the complexes were found to be non-ionic in nature. The bidentate behaviour of the dithiocarbamate ligand has been confirmed on the basis of the physico-chemical studies.

**Key Words:** Transition metal complexes, Dithiocarbamates, *p*-Toluidine.

### INTRODUCTION

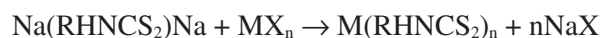
Intense research involving dithiocarbamate is currently going on due to the wide range of biological activities<sup>1-5</sup> exhibited by the complexes. Some of salts of dithiocarbamate derivatives exhibit interesting biological effects including anti-alkylation<sup>6,7</sup>, anti-HIV properties<sup>8</sup> and anti-tumor activity<sup>9</sup> against Leucemic cells. They are also used for cadmium intoxication<sup>10</sup>. Large quantities of water soluble dithiocarbamate complexes are used in various medical purposes<sup>11</sup>.

In the continued investigations<sup>12-16</sup> it was decided to focus attention in synthesizing metal complexes utilizing dithiocarbamate ligand derived from *p*-toluidine. This report presents synthesis and characterization of some metal complexes of first row transition series.

### EXPERIMENTAL

*p*-Toluidine, chlorides of chromium, manganese, iron, cobalt, nickel, copper, zinc (E. Merck) were used as received. Solvents (all BDH) were purified by standard methods<sup>17</sup> before use. Elemental analyses were performed at Regional Sophisticated Instrumentation Centre and Central Drug Research Institute, Lucknow, India. Sulphur was estimated gravimetrically by known procedure<sup>18</sup>. Infrared spectra in the region 4000-200 cm<sup>-1</sup> were recorded in nujol mull on Perkin-Elmer Model 1620 Fourier-Transform infrared spectrophotometer by Jamia Millia Islamia, New Delhi, India. Conductometric measurements were done on Systronics 321 conductivity bridge.

These metal dithiocarbamate complexes were synthesized by replacement reaction method which involves replacement reaction between the sodium salt of dithiocarbamate and metal salt.



**Synthesis of sodium dithiocarbamate of *p*-toluidine:** *p*-Toluidine, sodium hydroxide and carbon disulphide were taken in 1:1:1 molar ratios, respectively. To an ethanolic 0.1 M solutions of *p*-toluidine (10.72 g), 0.1 M CS<sub>2</sub> (6.03 mL) and aqueous 0.1 M NaOH (4.0 g) were added dropwise with constant stirring. The reaction mixture was stirred for 1 h. On completion of the reaction sodium *p*-toluidine dithiocarbamate was obtained, which was soluble in DMF.

**Synthesis of metal dithiocarbamate complexes:** In a molar ratio 1:2, 0.01 M solutions of respective metal salts (1.2594 g MnCl<sub>2</sub>, 1.2994 g CoCl<sub>2</sub>, 1.2972 g NiCl<sub>2</sub>, 1.3466 g CuCl<sub>2</sub> and 1.3636 g ZnCl<sub>2</sub>) were added to the 0.02 M solution containing 4.1 g sodium *p*-toluidine dithiocarbamate in DMF at room temperature. In a molar ratio 1:3, 0.01 M solutions of respective metal salts (1.5850 g CrCl<sub>3</sub> and 1.6234 g FeCl<sub>3</sub>) were added to 0.03 M solutions of 6.15 g sodium *p*-toluidine dithiocarbamate. The reaction mixture was stirred for 1 h. The solid thus formed was washed with diethyl ether and dried in air.

## RESULTS AND DISCUSSION

The replacement reaction method yielded dithiocarbamates of high purity as supported by their elemental analysis (Table-1). The colourless to colourful complexes were air and moisture stable at room temperature. The complexes were soluble in ethanol and benzene. These complexes were found to have melting points ranging from 205 to 240 °C.

The evidence regarding bonding and structures of these complexes has been deduced after thoroughly examining the observed frequencies characteristic of dithiocarbamate group in their infrared spectra. The IR spectra of solid complexes showed well-resolved and sharp bands (Table-2). The dithiocarbamate group being flexidentate ligand, can coordinate symmetrically involving both the sulphur atoms as well as unsymmetrically involving only one sulphur atom in complexation. The frequency modes  $\nu(\text{C-N})$  and  $\nu(\text{C-S})$  are diagnostic factors for the nature of dithiocarbamate moiety whether it is acting as monodentate or bidentate. The monodentate or bidentate nature of dithiocarbamate group in the ligand is reflected<sup>19,20</sup> in the  $\nu(\text{C-S})$  stretching frequency. In the case of bidentate behaviour, a single strong band appears in the region 1050-950 cm<sup>-1</sup>, while a doublet is expected in the region around 1000 cm<sup>-1</sup> for the monodentate one. Furthermore the thioureide band near 1500 cm<sup>-1</sup> implies a considerable double bond character in the SC-NRR' bond. In general,  $\nu(\text{C-N})$  frequency shows a blue shift in the complexes as compared to the respective dithiocarbamate ligands, if the dithiocarbamate group behaves as a bidentate ligand. For a monodentate dithiocarbamate moiety, this frequency should exhibit either no change in position or undergo a red shift with respect to the corresponding free ligand frequency. The  $\nu(\text{C-N})$  frequency in these dithiocarbamate complexes was observed in the range 1495-1475 cm<sup>-1</sup>. Since these frequency modes lie in between those associated with single C-N and double C=N bonds hence the partial double bond character of thioureide bond was confirmed<sup>21</sup> for all the complexes

studied. The  $\nu(\text{C-S})$  frequency occurred in the range 1015-1000  $\text{cm}^{-1}$  and the  $\nu(\text{M-S})$  stretching frequency appeared in the region 479-463  $\text{cm}^{-1}$ .

TABLE-1  
ANALYTICAL DATA AND OTHER PHYSICAL PROPERTIES OF  
*p*-TOLUIDINE DITHIOCARBAMATE COMPLEXES

Compounds (m.w.)	Yield (%)	m.p. (°C)	Colour	$\Lambda_m$ , $\text{ohm}^{-1}$ $\text{cm}^2 \text{mol}^{-1}$	Found (calculated) %				
					C	H	N	S	M
Na( <i>p</i> -Tol dtc) (205)	62	205	Colour less	–	46.72 (46.83)	3.87 (3.90)	6.91 (6.83)	31.27 (31.22)	– –
Cr( <i>p</i> -Tol dtc) <sub>3</sub> (597.99)	68	215	Green- blue	0.0897	48.03 (48.17)	4.03 (4.01)	7.03 (7.02)	32.26 (32.11)	8.65 (8.69)
Mn( <i>p</i> -Tol dtc) <sub>2</sub> (418.94)	58	222	Yellow	0.0560	45.74 (45.83)	3.81 (3.83)	6.71 (6.68)	30.46 (30.55)	13.28 (13.11)
Fe( <i>p</i> -Tol dtc) <sub>3</sub> (601.85)	60	230	Light yellow	0.0456	47.78 (47.85)	4.01 (3.99)	7.00 (6.98)	31.86 (31.90)	9.35 (9.28)
Co( <i>p</i> -Tol dtc) <sub>2</sub> (422.93)	78	220	Brown	0.0245	45.48 (45.40)	3.74 (3.78)	6.58 (6.62)	30.24 (30.27)	13.96 (13.93)
Ni( <i>p</i> -Tol dtc) <sub>2</sub> (422.71)	67	225	Light green	0.0178	45.33 (45.41)	3.81 (3.79)	6.63 (6.62)	30.21 (30.27)	14.02 (13.91)
Cu( <i>p</i> -Tol dtc) <sub>2</sub> (427.55)	68	240	Brown	0.2345	44.78 (44.91)	3.76 (3.74)	6.57 (6.55)	30.00 (29.94)	14.89 (14.86)
Zn( <i>p</i> -Tol dtc) <sub>2</sub> (429.37)	75	228	Colour less	0.7810	44.82 (44.72)	3.70 (3.73)	6.49 (6.52)	29.69 (29.81)	15.30 (15.22)

TABLE-2  
IR SPECTRAL BANDS ( $\text{cm}^{-1}$ ) OF *p*-TOLUIDINE  
DITHIOCARBAMATE METAL COMPLEXES

Complexes	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\nu(\text{M-S})$
Na( <i>p</i> -Tol dtc)	1475	1015	–
Cr( <i>p</i> -Tol dtc) <sub>3</sub>	1480	1005	479
Mn( <i>p</i> -Tol dtc) <sub>2</sub>	1486	1000	475
Fe( <i>p</i> -Tol dtc) <sub>3</sub>	1489	1002	466
Co( <i>p</i> -Tol dtc) <sub>2</sub>	1485	1003	463
Ni( <i>p</i> -Tol dtc) <sub>2</sub>	1483	1005	468
Cu( <i>p</i> -Tol dtc) <sub>2</sub>	1495	1008	475
Zn( <i>p</i> -Tol dtc) <sub>2</sub>	1487	1010	476

From these observations it is obvious that the dithiocarbamate group was coordinated to metal in bidentate fashion involving both the sulphur atoms. In  $\text{ML}_2$  type of complexes the metal was tetra-coordinated while in hexa-coordinated nature was showed by the metals in  $\text{ML}_3$ .

#### ACKNOWLEDGEMENTS

The authors are highly thankful to the Principal and the Chairman, Department of Chemistry, G.F. Post Graduate College, Shahjahanpur for providing necessary infrastructure.

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(Received: 19 May 2009;

Accepted: 25 November 2009)

AJC-8091