

SHORT COMMUNICATIONS

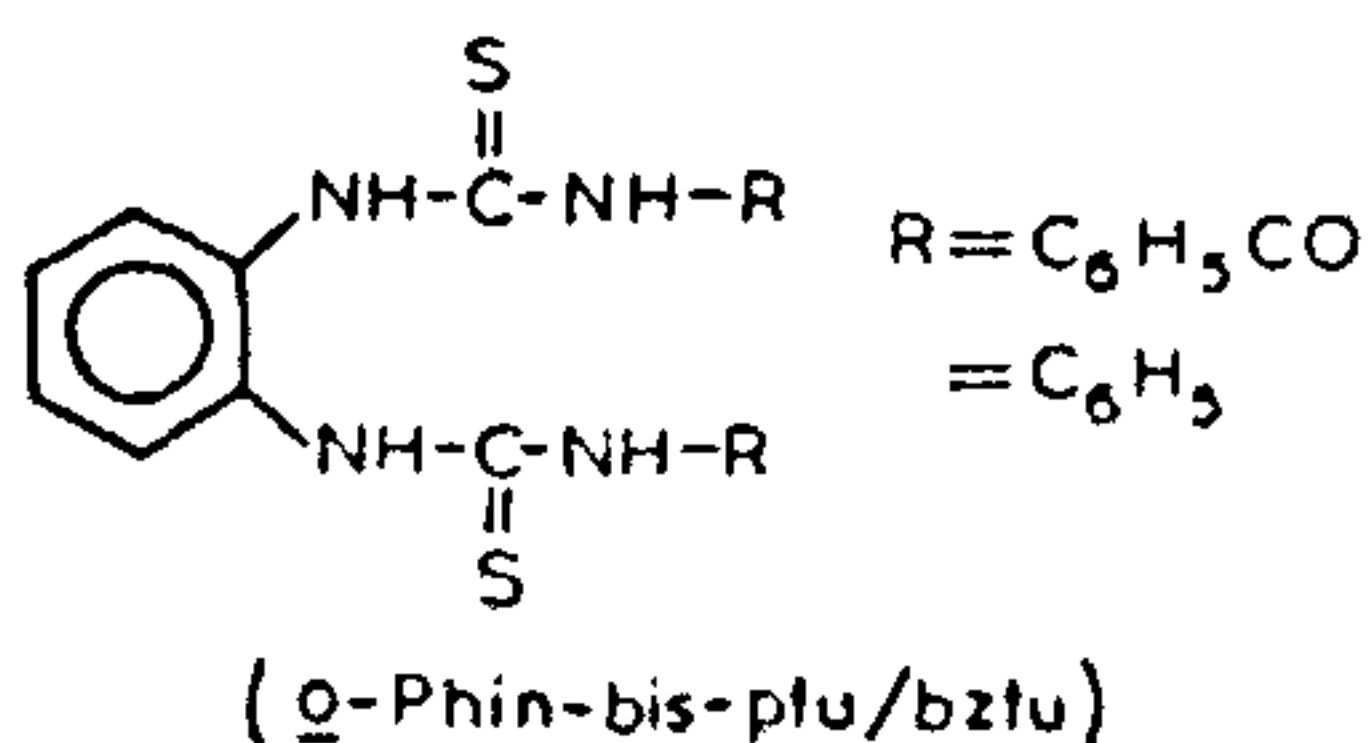
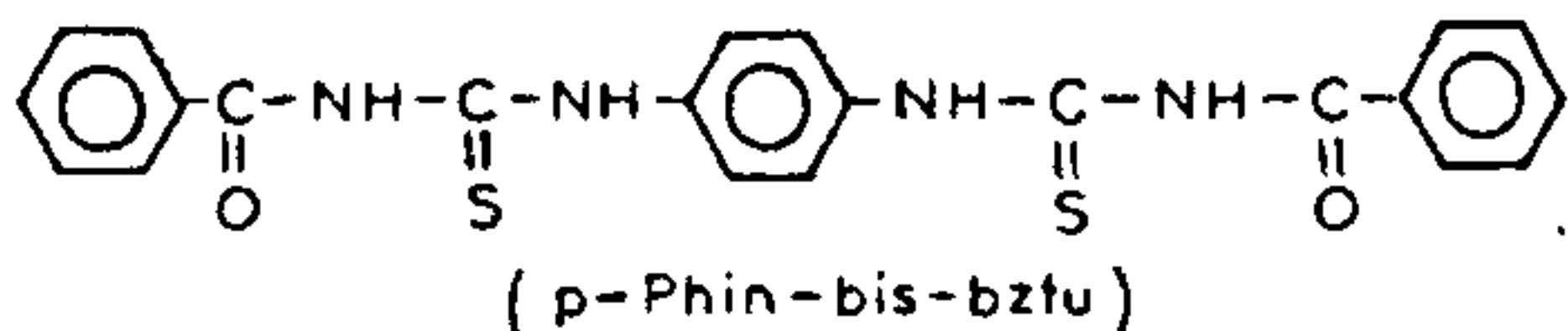
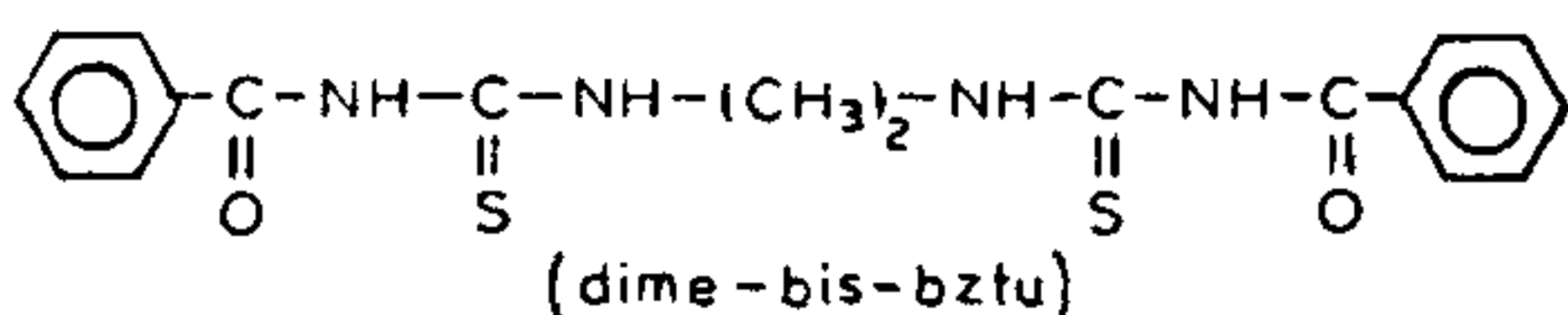
STUDIES ON THE TRANSITION METAL THIOCYANATE COMPLEXES WITH THIOUREAS CONTAINING S,S AND O,S,S,O DONOR SEQUENCES

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THE potential donor abilities of poly (alkylene) bis-aryl thioureas and the ambidentate behaviour of thiocyanate ions prompted us to synthesize some new substituted thioureas containing S,S and O,S,S,O donor sequence and their complexes with nickel(II) and cobalt(II) thiocyanates for which the existing literature is scanty^{1,2}. These complexes have been analysed and characterized by physicochemical techniques such as conductance, magnetic susceptibility, electronic and IR spectra and thermoanalytical studies.

The following bidentate ligands were synthesized following the published procedure³:— dimethylene-bis-benzoyl thiourea (Dime-bis-bztu, m.p. 220°C), *o*-phenylene-bis-phenyl thiourea (*o*-Phln-bis-ptu, m.p. 172°C), *o*-phenylene-bis-benzoyl thiourea (*o*-Phln-bis-bztu, m.p. 170°C) and *p*-phenylene-bis-benzoyl thiourea (*p*-Phln-bis-bztu, m.p. 178°C).



Both nickel(II) thiocyanate and cobalt(II) thiocyanate employed to synthesize the complexes were prepared by metathesis of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and KSCN in ethanol. The mixture of the metal thiocyanate (in ethanol) and the ligands (in *n*-butanol) in 1:1 mole ratio was refluxed for 2–3 hr on water bath when the solid complex separated. The solid thus obtained was filtered, washed with hot *n*-butanol and then with hot alcohol to remove excess ligand. Finally it was dried in vacuum over P_2O_5 . The complexes were analysed for nickel, cobalt, nitrogen and sulphur by standard methods⁴. For a few complexes the percentage of carbon and hydrogen was evaluated. The analytical data are presented in table 1.

The molar conductivity of the complexes in DMF (1×10^{-3} M) was determined using a conductivity bridge (ELICO) of cell constant 0.63. The infrared and far infrared spectra were recorded on PE-597 and Polytech FIR-30 instruments respectively. The magnetic susceptibilities of the complexes were determined by the Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant and the experimental magnetic susceptibilities were corrected for diamagnetism of the elements. The electronic spectra in nujol mull were recorded from 300 to 1500 nm on a UV-VIS spectrophotometer (Carl Zeiss DMR-21). The thermograms (TG/DTA/DTG) were recorded in the temperature range 0–1200°C on a MOM derivatograph at a heating rate of 10°C/min.

Both nickel(II) and cobalt(II) thiocyanates with the above thioureas yielded 1:1 complexes which were greenish-yellow and greenish-blue respectively. They are insoluble in common organic solvents but soluble in DMF and DMSO. The molar conductance value ($\lambda_M \sim 3-5 \text{ } \Omega \text{ cm}^2 \text{ mol}^{-1}$) suggests the nonionic nature of these complexes.

The different bands in near and far IR regions in the ligands and complexes were assigned according to published methods^{5,6}. The free ligand ν_{NH} bands in the region 3380–3160 cm^{-1} show a slight blue shift ($\sim 5-10 \text{ cm}^{-1}$) and considerable broadening on complexation which is attributed to the intense intramolecular hydrogen bonding of the type $\text{C}=\text{O} \dots \text{H}-\text{N}$ and $\text{C}=\text{S} \dots \text{H}-\text{N}$ ⁷. The positive shift in the ν_{NH} band in the present complexes is indicative of the double bond character of $\text{C}=\text{N}$ suggesting the non-coordination of nitrogen to the metal. The $\nu_{\text{C}=\text{O}}$ vibrations pertaining to the benzoyl group of the ligands (1630–1660 cm^{-1}) show positive shift (1640–

Table 1 Physical and analytical data Ni(II) and Co(II) complexes

Complex	μ_{eff} (B.M.)	% C	% H	% S	% N	% Ni/Co
Ni(dime-bis-bztu)(SCN) ₂	dia	42.56 (42.79)	3.15 (3.23)	22.40 (22.84)	14.76 (14.97)	10.28 (10.45)
Ni(o-phln-bis-ptu)(SCN) ₂	3.51	47.45 (47.75)	3.19 (3.28)	23.04 (23.17)	14.95 (15.18)	10.48 (10.60)
Ni(o-phln-bis-bztu)(SCN) ₂	dia	—	—	20.86 (21.04)	13.60 (13.79)	9.48 (9.63)
Ni(p-phln-bis-bztu)(SCN) ₂	3.34	—	—	20.83 (21.04)	13.68 (13.79)	9.49 (9.63)
Co(dime-bis-bztu)(SCN) ₂	2.53	—	—	22.69 (22.83)	14.79 (14.96)	10.40 (10.49)
Co(o-phln-bis-bztu)(SCN) ₂	4.64	47.08 (47.29)	2.82 (2.98)	20.90 (21.03)	13.70 (13.78)	9.49 (9.66)

Figures in parentheses indicate calculated values.

1670 cm⁻¹) in the complexes. This rules out the possibility of coordination through carbonyl oxygen (>C=O)⁸. A medium sharp band in the region 750–795 cm⁻¹ is assigned to $\nu_{\text{C}=\text{S}}$ vibration coupled with $\nu_{\text{C}=\text{N}}$ (slight contribution) in the ligands. This band suffers reduction in intensity and becomes a medium broad band. It also undergoes a negative shift of the order 15–30 cm⁻¹ during coordination. Further, another medium sharp band in the region 660–690 cm⁻¹ for ligands is indicative of $\nu_{\text{C}=\text{S}}$ vibration. This also undergoes a negative shift of the order of 10–20 cm⁻¹ with simultaneous intensity reduction of the band during complexation. Thus it is suggestive of 'S' coordination of thioureas to the central metal ion. The nature of thiocyanate bonding ('S' or 'N') can be judged from ν_{CS} and ν_{CN} vibrations⁶. With the exception of Co (Dime-bis-bztu) (NCS)₂, all other complexes involve S bonding of thiocyanate as supported by ν_{CN} (2100–2180 cm⁻¹) and ν_{CS} (690–720 cm⁻¹) vibrations. However the former complex exhibits ν_{CN} band at a lower (~2060 cm⁻¹) and ν_{CS} band at a higher (~795 cm⁻¹) frequency which clearly reveal N bonding for thiocyanate^{9,10}. This has been further confirmed by far IR spectra for $\nu_{\text{M}-\text{S}}$ (316–310 cm⁻¹) and δ_{NCS} (440–455 cm⁻¹) in the case of complexes other than the said cobalt complex. However the appearance of δ_{NCS} (475–480 cm⁻¹) justifies N bonding for the cobalt complex.

Electronic spectra in solid state were recorded for the above complexes. The Ni(II) thiocyanate thioureas exhibit three bands ν_1 (8600–9800 cm⁻¹, $^3T_{2g} \leftarrow ^3A_{2g}$), ν_2 (15800–16400 cm⁻¹, $^3T_{1g}(\text{F}) \leftarrow ^3A_{2g}$) and ν_3 (25000–26000 cm⁻¹, $^3T_{1g}(\text{P}) \leftarrow ^3A_{2g}$) out of which the first band has been equated to 10 Dq¹¹. The

spectral parameters B(870–940 cm⁻¹), β (0.83–0.90) and the ratio ν_2/ν_1 (1.68–1.78) illustrate the octahedral geometry of Ni(II) complexes¹². The two bands ν_2 (6900 cm⁻¹, $^4T_1 \leftarrow ^4A_2$) and ν_3 (16900 cm⁻¹, $^4T_1 \leftarrow ^4A_2$) observed for cobalt complexes yield 10 Dq (396 cm⁻¹) and β (0.81) suggest tetrahedral nature. Further, the symmetry of the complexes is confirmed from μ_{eff} values of Ni 3.3 to 3.45 B.M ($\mu_s = 2.84$ B.M) and of Co 4.64 B.M ($\mu_s = 3.87$ B.M) (c.f. table 1). It is to be pointed out that SCN group may act as a bridge in the octahedral Ni(II) complexes. The diamagnetic nature of other nickel(II) (Nos.1 and 3) and the reduced paramagnetism observed for Co(II) complexes (2.53 B.M for complex⁵) support a square planar geometry.

The thermoanalytical curve of one representative complex Ni(o-Phln-bis-bztu) (NCS)₂ has been examined. The observed percentage weight losses are 72.5% [71.3% for loss of one ligand at 400°C] and 91.5% [90.4% for loss of one ligand and 2 SCN groups at 720°C] and duly support the composition of the complex as established from analytical data.

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ESTIMATION OF PALLADIUM(II) USING 4-AMINO-3-MERCAPTO-1, 2, 4-TRIAZINE -(4H)-5-ONE AS REPLACING REAGENT

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A simple, rapid, accurate and selective complexometric method is proposed for the determination of palladium(II). Palladium(II) with associated diverse metal ions can be first complexed with EDTA and the Pd-EDTA complex can be selectively decomposed using demasking agents¹⁻⁶. In some of these methods the liberation of EDTA is not rapid because it requires heating. Some other methods need extraction or involve precipitation during titration, the end point consequently being not distinct. In this paper, the use and advantages of 4-amino-3-mercapto-1,2,4-triazine -(4H)-5-one (AMT) as a selective demasking agent is reported for the complexometric determination of Pd(II).

The speciality of the reagent is that it does not form any precipitate with either Pd(II) the metal ion to be estimated, or Pb(II) the titrant for EDTA under the experimental conditions. This facilitates sharp detection of the end point without necessitating the use of other chemicals.

All chemicals used are of AR or chemically pure grade.

To an aliquot of the neutral solution (containing 0.5–5 mg) of Pd(II), an excess of EDTA solution is added. The pH of the solution is adjusted to between 5 and 6 by adding acetic acid–sodium acetate buffer. The excess of EDTA is back-titrated

against the standard lead nitrate solution to the sharp colour change of the xylenol orange indicator from yellow to red. To this is added 0.5% AMT solution in acetone-water mixture in slight excess over the molar ratio of 1:2. The contents are mixed well. The liberated EDTA is titrated with the lead nitrate solution to the same end point as before. The second titre value is equivalent to Pd(II) present in the aliquot. Reproducible and accurate results are obtained with a relative error of < 0.4% and standard deviation of < 0.01. Interference of many common metal ions and rare-earth metal ions is also studied.

The results of determination of palladium(II) from its solution show that reproducible and accurate values can be obtained. The effect of common metal ions on the quantitative determination of Pd(II) was studied with aliquots containing 2.753 mg of Pd(II). Cations like Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III), Bi(III), Al(III), La(III), Rh(III), Ru(III), Au(III), Cr(III), Zr(IV) and Ti(IV) show no interference. However cations like Ag(I), Fe(II), Sn(II), Hg(II) and Tl(III) show interference which can be overcome by using appropriate secondary masking agents.

The quantitative displacement of EDTA from Pd-EDTA complex by AMT indicates that the Pd-AMT complex is more stable than the Pd-EDTA complex at room temperature and that EDTA is released spontaneously. However for the complete release of EDTA, the AMT reagent is required to be added slightly in excess of the stoichiometric ratio of 1:2 for the metal:reagent. A large excess of the reagent does not show any adverse effects on the results of the estimation.

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