mixing the reactants remained stable during the course of the titration, and the formation of precipitates were observed only beyond $pH = 9.4$.

The dissociation constants, pK_1 and pK_2 of cysteine at 24° were 8.05 and 10.30 respectively. These are in good agreement with the published values[20,21]. The formation constants of the mixed ligand chelates are given in Table 1. The value of $\log K_{M-DPY-Cys}^{M-DPY}$ and $\log K_{M-Phe-Cys}^{M-Phe}$ of the metal complexes is less than the corresponding values for metal-cysteine ($\log K_1$) complexes because of statistical factors. In binary systems cysteine coordinates to the metal through amino and sulphydryl group[10] but in ternary systems as in our case, coordination seems to occur through amino and carboxylate ion as indicated by the lower values of stability constants. Such a lower value is also reported in the case of metal alanine complex ($\log K_1 = 5.94$) where also, the coordination occurs through amine and carboxylate ion[2].

TABLE 1—FORMATION CONSTANTS OF MIXED LIGAND CHELATES AT 24° ($\mu = 0.1M$, NaClO₄)

Metal	$\log K_{M-DPY-Cys}^{M-DPY}$	$\log K_{M-Phe-Cys}^{M-Phe}$	$\log K_1^{*}$ (M-Cys)
Co(II)	4.45	4.30	9.30
Ni(II)	5.55	5.45	9.64
Cu(II)	6.00	5.90	Unstable
Zn(II)	5.35	5.05	9.86
Pd(II)	5.60	5.45	—

* Literature value.

The presence of a strong band at 3400 cm⁻¹ and the shifting of a band from 1700 cm⁻¹ (cysteine) to ≈1600 cm⁻¹ (in complexes) in the ir spectra of complexes also indicated the coordination of the secondary ligand through amine and carboxylic group.

The electronic spectra of solutions of diamagnetic Ni(II) complexes in 50% ethanol gave five bands at 41000, 33500, 32500, 31000 and 26500 cm⁻¹ corresponding to $^1A_{1g} \rightarrow ^1E_u$, $^1A_{1g} \rightarrow ^1A_{2u}$, $^1A_{1g} \rightarrow ^1B_{1u}$, $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1A_{2g}$ transitions respectively. Similarly, the solutions of diamagnetic Pd(II) complexes gave the bands at 38000, 30000, 28500 and 22500 cm⁻¹ corresponding to the $^1A_{1g} \rightarrow ^1B_u$, $^1A_{1g} \rightarrow ^1E_g$, $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1A_{2g}$ transitions respectively. The observed magnetic moment value 1.85 B.M. of Cu(II) complexes was very close to that predicted for spin only value. Three bands at 21500, 20000 and 16000 cm⁻¹ were observed corresponding to the transitions, charge transfer, $^2B_{1g} \rightarrow ^2E_g$ and $^2B_{1g} \rightarrow ^2A_{1g}$ respectively. Thus the complexes of Ni(II), Pd(II) and Cu(II) were found of square planer structure. In the case of Co(II) complexes, the value of magnetic moment was found to be 4.50 B.M. which is usally encountered in tetrahedral cobalt(II) complexes[22]. Secondly, their electronic spectra gave the bands at 25000 and 32500 cm⁻¹ which correspond to $^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$ and $^4A_{2g}(F) \rightarrow ^4T_{1g}(P)$ respectively.

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Infrared Spectra of Some New Dithiocarbamates

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THE present communication describes synthesis and infrared spectra of a new series of dithiocarbamates, $(C_6H_5CH_2)(R)NCS_2^-$, viz.,

R = H, benzyldithiocarbamate (BzHNCS₂⁻),

R = CH₃, benzylmethyldithiocarbamate
(BzMeNCS₂⁻),

R = C₂H₅, benzylethyldithiocarbamate
(BzEtNCS₂⁻),

R = C₃H⁷, benzyl*iso*propyldithiocarbamate
(BziPrNCS₂⁻),

and R = C₆H₅CH₂, dibenzyldithiocarbamate
(Bz₂NCS₂⁻).

Variation in $v(CN)$ with the change in R group has been discussed. A comparison has also been

TABLE 1—ANALYTICAL DATA AND IMPORTANT INFRARED BANDS (cm⁻¹)

Compound	m.p. °C	C% Found (Calcd.)	H% Found (Calcd.)	N% Found (Calcd.)	ν(C=N)	ν(CSS)ssy	ν(CSS)sym
1. BzHNCS₂NH₄	126	47.91 (48.00)	5.88 (6.00)	14.30 (14.00)	1361 s	920 vs	684 vs
2. Bz₂NCS₂K.3H₂O	101	49.27 (49.32)	5.51 (5.48)	3.73 (3.84)	1442 vs	972 vs	700 vs
3. BzMeNCS₂Na.3H₂O	250-252	39.39 (39.57)	5.80 (5.86)	5.03 (5.13)	1470 s	990 vs / 952 vs / 972 vs	700 vs
4. BzEtNCS₂NH₄	113	52.69 (52.63)	7.33 (7.02)	12.19 (12.28)	1447 s	958 vs / 940 vs	699 vs
5. BziPrNCS₂Na.3H₂O	68-70	43.77 (43.85)	6.71 (6.64)	4.53 (4.65)	1432 vs	962 vs	694 s
6. Me₂NCS₂Na (Ref. 3)	—	—	—	—	1503 s		
7. Et₂NCS₂Na (Ref. 3)	—	—	—	—	1477 s		
8. PhHNCS₂NH₄ (Ref. 4)	—	—	—	—	1325 s		

made with ν(CN) values for dialkyldithiocarbamates and phenyldithiocarbamate.

Preparations of the dithiocarbamates : The amines used for the preparation of dithiocarbamates were obtained from Aldrich Chemical Co., Dorset, and were used as received. The dithiocarbamates were prepared as the sodium, potassium or ammonium salts as described below.

(i) *Ammonium benzyldithiocarbamate (BzHNCS₂-NH₄) :* Benzylamine (0.1 mole) was slowly run in 15 min with vigorous stirring into an ice cooled solution containing CS₂ (0.1 mole) and concentrated ammonia (sp. gr. 0.89 ; 0.1 mole) maintaining the temperature of the reaction mixture between 0-5°. A white crystalline product was obtained, which was washed first with a little cold water, then several times with solvent ether and finally suction dried. The product was recrystallised from acetonechloroform mixture. Yield, 70%.

(ii) *Potassium dibenzyldithiocarbamate trihydrate* (Bz₂NCS₂K.3H₂O),

(iii) *Sodium benzylmethyldithiocarbamate trihydrate* (BzMeNCS₂Na.3H₂O),

(iv) *Ammonium benzylethyldithiocarbamate* (BzEtNCS₂NH₄),

(v) *Sodium benzylisopropyldithiocarbamate trihydrate* (BziPrNCS₂Na.3H₂O) :

An aqueous solution containing 0.1 mole each of the base (NaOH/KOH/NH₄OH) and the amine dissolved in minimum amount of water was cooled to 15° in ice cooled water (to 0° in an ice bath in the case of benzylmethyl amine). To this cooled solution 0.1 mole of CS₂ was added dropwise with stirring. After about half an hour the whole mass solidified. The white solid mass was dried in air and dissolved in minimum quantity of pure acetone. An excess of carbon tetrachloride was added to this solution when a shining white compound separated out. It was filtered and suction dried. The product was recrystallised from acetone-chloroform mixture. Yield, 70-75%.

Analytical data alongwith other physical characteristics of the dithiocarbamates are given in Table 1.

Infrared spectra : The infrared spectra of the dithiocarbamates were recorded in KBr pellets on a Perkin Elmer 621 recording spectrophotometer in the range 4000-200 cm⁻¹ as well as on Perkin Elmer 137 infracord spectrometer in the range 4000-700 cm⁻¹. Important infrared spectral bands are given in Table 1. $\nu_{(CN)}$ for Me₂NCS₂Na, Et₂NCS₂Na and PhHNCS₂NH₄ are also given for the sake of comparison.

The structure of the dithiocarbamate anion can be represented by the following resonating forms :

(a)   (b)   (c)
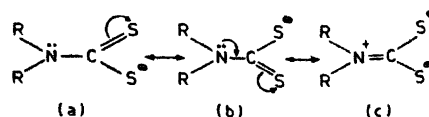
The extent to which the resonance form (c) contributes to the overall dithiocarbamate structure determines the extent of double bond character of the (C−N) bond².

A perusal of the data in Table 1 reveals that CN stretching frequencies for the present dithiocarbamates are slightly lower than those for dialkyldithiocarbamates and much higher than those of phenyldithiocarbamate. This observation may be explained on the basis of the electronic effects shown below :

(1)   (2)   (3)
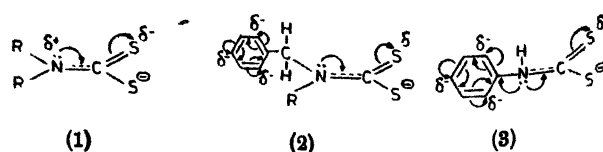
In dialkyl dithiocarbamates (1) R groups release electrons through +I inductive effect and the lone pair on the nitrogen atom becomes more available for the formation of double bond. In aryldithiocarbamates (3), on the other hand, there is a very large reduction in the double bond character of the (CN) bond due to electron withdrawing effect on the phenyl ring. In the present dithiocarbamates (2), although −CH₂− of the benzyl group releases electrons through hyperconjugation into the

π-electron system of the phenyl ring, the overall -I inductive effect of the benzyl group is not significant as in the case of phenyl group, because the latter is directly attached to the nitrogen atom carrying a lone pair of electrons. Thus, the double bond character in case of these ligands would be higher than in the phenyldithiocarbamates and lower than in the dialkyldithiocarbamates.

Also, the (CN) bond order in the present dithio-carbamates is BzMeNCS$_2$ > BzEtNCS$_2$ > Bz$_2$NCS$_2$ > Bz-iPrNCS$_2$ > BzHNCS$_2$. The Bz group being common, the order can be explained on the basis of electronic effects of the other group, viz. H, Bz, Me, Et and iso-Pr. When H of the benzyldithiocarba-mate is replaced by benzyl or alkyl group, the (CN) bond order is increased due to the electron donating tendency of the alkyl groups. If the electronic effects were purely inductive in nature, the (CN) bond order should increase as the size of the alkyl group increases. But in case of BzMedtc, BzEtdtc and Bziso-Prdtc a reverse trend is observed i.e. the (CN) bond order decreases as we proceed from methyl to isopropyl through ethyl. In the dithio-carbamates, as the alkyl groups are attached to the partially double bond nitrogen, hyperconjugation is expected to be operative and the electron releasing ability can be in the order Me > Et > iso-Pr. The position of Bz$_2$dtc can similarly be explained. However, kinematic effects due to increasing mass of the alkyl group have also been suggested to be responsible[5,6].

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Stability Constants of Fe(II), Co(II), Ni(II), Cu(II) and Cd(II) Complexes of 2, 2'-Dipyridyl-2-Pyrimidylhydrazone

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2, 2'-Dipyridyl-2-pyrimidylhydrazone (DPPmH) was employed by Singh[1] for spectrophotometric determination of various transition metals. In this paper the stepwise stability constants of binary complexes of DPPmH at pH 9.0 are reported. At pH 9.0 these metals are simultaneously deter-minable[2,3] and hence pH 9.0 is selected for present studies. The Yatsimirskii's[4,5] and Lenden's[6] graphical extrapolation methods were applied with necessary modification[7] to calculate the values of step-wise stability constants. The experiments were performed at constant temperature $30\pm1°$.

Experimental

2, 2'-Dipyridyl-2-pyrimidylhydrazone (DPPmH) was prepared as described earlier[1]. $0.002M$ reagent solution in 40% ethanol-water was used. Solutions of Fe(II), Co(II), Ni(II), Cu(II) and Cd(II) were prepared and standardised as reported in earlier communications[2,3]. 1.0% Ascorbic acid in distilled water was used to prevent oxidation of Fe(II).

Apparatus : Beckman model DU 2 spectro-photometer with quartz cells of 10 mm light path was used for all photometric measurements. An ELICO pH-meter with glass and saturated calomel electrodes was employed for pH adjustments. All measurements were made at $30\pm1°$ using thermostat.

Procedure : A solution containing a known quantity of metal ion [Fe(II) = $3.0 \times 10^{-5}M$; Co(II) = $2.0 \times 10^{-5}M$; Ni(II) = $8.0 \times 10^{-5}M$; Cu(II) = $1.0 \times 10^{-5}M$ and Cd(II) = $7.5 \times 10^{-5}M$] varying quantity of DPPmH solution and 2 ml 1% ascorbic acid was adjusted to pH 9.0 in 40% ethanol-water, total volume being 25 ml. The absorbances were noted at respective wavelengths of maximum absorption [580, 460, 430 and 440 nm for Fe(II), Co(II), Ni(II), Cu(II) and Cd(II), respectively] against the reagent as a blank. The concentration of complex formed was computed from the appropriate calibration curve.

TABLE 1—STABILITY CONSTANTS FOR DPPmH COMPLEXES AT pH 9.0

	Yatsimirskii's method Fe(II)-DPPmH	Leden's method	Mole ratio method
log K$_1$	5.34	5.08	—
log K$_2$	4.95	4.40	—
log β_2	10.29	9.48	10.13
	Co(II)-DPPmH		
log K$_1$	4.79	4.78	—
log K$_2$	4.52	4.52	—
log β_2	9.31	9.30	9.84
	Ni(II)-DPPmH		
log K$_1$	5.67	5.70	—
log K$_2$	5.40	5.45	—
log β_2	11.07	11.15	11.61
	Cu(II)-DPPmH		
log K$_1$	5.25	5.16	—
log K$_2$	4.97	4.97	—
log β_2	10.22	10.13	10.88
	Cd(II)-DPPmH		
log K$_1$	6.26	6.30	—
log K$_2$	5.97	6.05	—
log β_2	12.23	12.35	12.90