N,N-Dibromobenzenesulfonamide as an Analytical Reagent: Determination of Thiocyanate and Cyanide Ions in Metal Complexes and Salts and Thiosemicarbazide Alone and in Its Metal Complexes

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INTRODUCTION

As a part of our broad program of introducing new redox titrants in general and aromatic sulfonyl haloamines in particular, to develop rapid and accurate analytical procedures for determining a variety of industrially and biologically important organic and inorganic substances in solution (*1, 3–25, 28, 30*) we have introduced a new reagent, *N,N*-dibromobenzenesulfonamide or dibromamine-B ($C_6H_5SO_2NBr_2$, abbreviated as $RNBr_2$ or DBB) (*22*) as an addition to the class of N-haloamines. The haloamines are known to behave as halogenating or oxidizing agents, depending on the pH of the medium and nature of the reductants.

Thiocyanates find a number of industrial applications in photography, printing, dyeing textiles, medicine, and freezing mixtures, in the manufacture of synthetic dyestuffs, sulfocyanides, thioureas, and mustard oil, and as reagents in analytical chemistry. The analytical procedures reported so far (*3, 6, 8, 24, 28*) for determining NCS^- ion include the use of

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hypohalite, bromine, iodine, iodate, hydrogen peroxide, and some aromatic sulfonyl haloamines.

Cyanides have a number of industrial applications such as in the extraction of noble metals in photography and in the preparation of insecticides and cyanogen derivatives. Silver nitrate, alkaline permanganate, iodine, lead tetraacetate, and organic sulfonyl haloamines are some of the reagents used for estimating cyanide ion in solution (4, 8, 13, 24, 28).

Thiosemicarbazide (TSC) is used in the characterization of aldehydes, ketones, and polysaccharides and as a metal complexing agent. The oxidants employed for its determination include alkali metal hypohalites, lead tetraacetate, and some aromatic sulfonyl haloamines (5, 7, 14, 15, 17, 21, 25, 28).

This paper reports the preparation of DBB and its characterization from mass spectrum, infrared (ir), and Fourier transform nuclear magnetic resonance-^{1}H and -^{13}C (FT-NMR-^{1}H and -^{13}C) spectral data and the analytical procedure developed for determining thiocyanate and cyanide ions in metal complexes and salts and TSC alone and in its metal complexes.

The proposed analytical procedure is simple, elegant, and reproducible under the experimental conditions described. An added advantage is that the technique can be employed for computing the number of CN⁻, NCS⁻, and TSC ligands present in the respective complexes.

MATERIALS AND METHODS

Potassium thiocyanate (AR, E. Merck) was dried at 150°C and its purity was checked. Metal thiocyanates LiNCS, NaNCS, $Cd(NCS)_2$, $Zn(NCS)_2$, $Ni(NCS)_2 \cdot 0.5H_2O$, $Ba(NCS)_2 \cdot 2H_2O$, $Pb(NCS)_2$, and $UO_2(NCS)_2 \cdot 3H_2O$, and complexes $K_2Cd(NCS)_4 \cdot 2H_2O$, $K_2Zn(NCS)_4 \cdot 4H_2O$, $K_4Ni(NCS)_6 \cdot 4H_2O$, $KUO_2(NCS)_3 \cdot 2H_2O$, and $K_4Pb(NCS)_6$ were prepared (3) and their purity was checked by elemental analyses. AR grade KCN and NaCN (Reanal, Hungary) were used without further purification. The salts AgCN and $Zn(CN)_2$ and complexes $KAg(CN)_2$ and $K_2Zn(CN)_4$ were prepared (13). E. Merck thiosemicarbazide was recrystallized from aqueous solution. Platinum and palladium complexes were prepared from $H_2PtCl_6 \cdot xH_2O$ and $PdCl_2$ (Johnson–Mathey, Ltd., London). The following thiosemicarbazide (L) complexes were prepared by methods reported elsewhere (5, 7, 17, 26, 27): ML_2X_2, where M = Zn, Cd, Ni, or Hg, X = Cl, NO_3, ClO_4, or ½ SO_4; cis- and trans-PtL_2Cl_2 and PtL_2X_2, where X = Br, I, CN, NCS, or NO_3; cis- and trans-$PdL_2(NO_3)_2$; PdL_2X_2, where X = Cl, Br, I, or NCS; and neutral complexes $M(L-H)_2$, where M = Ni, Pt, or Pd. The complexes were recrystallized from aqueous solution and characterized by their elemental analyses and ir spectra (26, 27).

Preparation of dibromamine-B. This was prepared by the bromination of CAB (22). The latter was obtained by bubbling chlorine gas through a

solution of benzenesulfonamide in 4 M NaOH over a period of 1 hr at 70°C. The recrystallized CAB (30 g) was dissolved in water (560 ml) and liquid bromine (6 ml) was added dropwise from a buret with constant stirring. The yellow precipitate of DBB formed was thoroughly washed with water, filtered under suction, and dried in a vacuum disiccator. The available bromine of DBB was determined by iodometry.

Spectral data of dibromamine-B. The ir spectra of CAB and DBB (in KBr) are almost the same, but DBB was further characterized by FT-NMR-^{13}C and -^{1}H spectra (obtained on a Bruker WH 270-MHz NMR spectrometer, Switzerland). The proton-noise-decoupled ^{13}C spectrum (measured in methanol-d solvent with tetramethylsilane, TMS, as the internal standard) showed the following chemical shifts (δ in ppm): C-1 atom attached to S atom (143.285); C-2,2' atoms (129.491); C-3,3' atoms (126.205); C-4 atom (132.901). The ^{1}H spectrum (measured in CDCl$_3$ solvent, using TMS as the internal standard) showed three distinct peaks centered around 8.15 (doublet), 7.81 (triplet), and 7.67 δ (triplet) due to o-, m-, and p-protons, respectively. The PMR signals due to m- and p- protons appear as a multiplet for the parent compound CAB, but the peaks are well resolved for the covalent compound DBB. Downfield shifts of 0.3 and 0.1 δ have been observed for the o- and m- protons in DBB, with $J_{o,m}$ = 8.0 Hz. Comparison of the CMR spectra of DBB and CAB indicates an upfield shift for C-1 ($\sim$0.8 ppm) and a downfield shift of $\sim$2 ppm for the other carbon atoms of the former. In DBB, the introduction of a second halogen atom thus increases the electron density around C-1 (carbon attached to the hetero atom) and it is likely that DBB may function as a better oxidizing agent than CAB.

Reductant solutions. Triply distilled water was used in preparing the solutions. Aqueous solutions ($\sim$2 mg/ml) of thiocyanates, soluble cyanides (KCN and NaCN), complex cyanides (KAg(CN)$_2$ and K$_2$Zn(CN$_4$), and TSC complexes were prepared, while Pb(NCS)$_2$ was dissolved in 2 N acetic acid. Aqueous KCN (0.025 M and the solution should be standardized) was used as solvent (*4, 8*) for the insoluble cyanides, AgCN and Zn(CN)$_2$.

Dibromamine-B solution. An approximately 0.025 M ($\sim$0.1 N) solution of DBB was prepared by dissolving 7.88 g in a liter of water-free acetic acid. It was then standardized by the iodometric method and stored in amber colored bottles. Reagents of acceptable grades of purity were used in preparing other solutions. To avoid exposure to the poisonous and toxic HCN gas formed by the cyanide salts and complexes in acid medium, experiments were performed in a chemical hood.

Preliminary investigations. Known amounts of the reductant solutions were added to a known excessive volume (25 ml) of 0.1 N oxidant in a glass-stoppered Erlenmeyer flask. The reaction mixtures were allowed to

TABLE 1

EXTENT OF OXIDATION OF POTASSIUM THIOCYANATE AND POTASSIUM CYANIDE WITH
DIBROMAMINE-B (DBB) IN PARTIALLY AQUEOUS MEDIUM

Time (min)	μmol of DBB consumed[a] / μmol of KNCS taken[b]	Number of electrons changing per mol of KNCS	μmol of DBB consumed[a] / μmol of KCN taken[c]	Number of electrons changing per mol of KCN
1	1.580	6.32	0.328	1.31
5	1.938	7.75	0.398	1.59
15	2.000	8.00	0.498	1.99
30	2.000	8.00	0.503	2.01
45	2.000	8.00	0.498	1.99

[a] DBB taken: 673.333 μmol.
[b] KNCS taken: 102.9 μmol.
[c] KCN taken: 147.0 μmol.

stand for different intervals of time at laboratory temperature (27 ± 3°C) with occasional shaking. The excess oxidant left unconsumed was then iodometrically titrated with standard thiosulfate.

The rates of oxidation of aqueous solutions of KNCS, KCN, and TSC with DBB are shown in Tables 1 and 2. It is seen from Table 1 that NCS⁻ ion undergoes an 8-electron change and CN⁻ is oxidized with a 2-electron change. Table 2 shows that the TSC molecule undergoes an oxidation with a 12-electron stoichiometry. It is seen that the required stoichiometries can be attained in about 15 min.

RECOMMENDED PROCEDURE

Add aliquots of reductant solutions to a known volume (50–60% excess) of 0.1 N DBB solution and set the reaction mixture aside with

TABLE 2

EXTENT OF OXIDATION OF THIOSEMICARBAZIDE (TSC) WITH DIBROMAMINE-B (DBB)
IN PARTIALLY AQUEOUS MEDIUM

Time (min)	μmol of DBB consumed[a] / μmol of TSC taken[b]	Number of electrons changing per mol of TSC
1	2.743	10.97
5	2.850	11.62
15	2.998	11.99
30	2.998	11.99
45	2.998	11.99

[a] DBB taken: 675.9 μmol.
[b] TSC taken: 109.72 μmol.

occasional shaking for about 15 min. Then add an excess amount of 10% KI solution and titrate the liberated iodine with 0.05 N sodium thiosulfate (V_1, ml) by adding 1 ml of starch solution near the end point. Run a blank with DBB solution alone (V_2, ml).
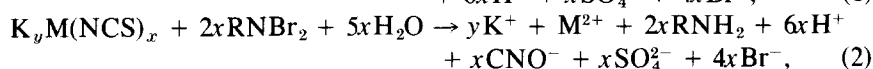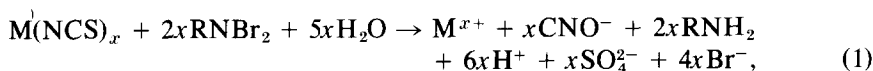
The amount of the reductant (X, μmol) in the test solution is given by $X = 10^3 \, N(V_2 - V_1)/E$, where N is the normality of thiosulfate and E is the number of electrons changing per molecule of the reductant. For $KAg(CN)_2$ and $K_2Zn(CN)_4$, $E = 4$ and 8, respectively. For Cd, Ni, Pb, Zn, Ba, and UO_2 thiocyanates, $E = 16$, while for complex thiocyanates of U, Zn, Cd, Ni, and Pb, $E = 24$, 32, 32, 48, and 48, respectively. For TSC complexes of the type ML_2X_2 or $M(L-H)_2$, $E = 24$. $PtL_2(CN)_2$ is oxidized with a 28-electron change, due to the presence of two CN^- ions. For $PtL_2(NCS)_2$ and $PdL_2(NCS)_2$, $E = 40$, since NCS^- ion is oxidized under these conditions.

Calculation of recovery with insoluble cyanides. Add aliquots (a, ml) of insoluble cyanides in 0.025 M KCN to a known excessive (50–60% excess) volume of DBB (V, ml). Set aside the reaction mixtures for about 15 min, with occasional shaking. Determine the unconsumed oxidant (V_3, ml). Add a ml of 0.025 M KCN to V ml of DBB under the same conditions as above. Estimate the unreacted oxidant by iodometric titration with thiosulfate (V_4, ml). Then the amount (Y, μmol) of insoluble cyanide in the sample solution is given by $Y = 10^3 \, N(V_4 - V_3)/E$, where $E = 2$ and 4 for AgCN and $Zn(CN)_2$, respectively and N is the normality of thiosulfate.
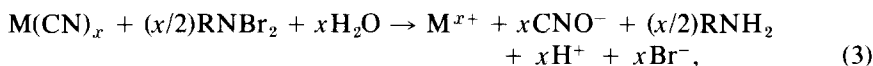
RESULTS AND DISCUSSION

Tables 1 and 2 give the time dependence of the oxidation of NCS^-, CN^-, and TSC by excess DBB in aqueous acetic acid medium. It follows from these tables that the reactions proceed quantitatively and stoichiometrically with the consumption of 8, 2, and 12 eq of the oxidant per mole of NCS^- and CN^- ions and TSC, respectively.

The stoichiometric oxidation of thiocyanate ion in metal salts and complexes with DBB is shown in

$$M(NCS)_x + 2xRNBr_2 + 5xH_2O \rightarrow M^{x+} + xCNO^- + 2xRNH_2$$
$$+ \, 6xH^+ + xSO_4^{2-} + 4xBr^-, \qquad (1)$$
$$K_yM(NCS)_x + 2xRNBr_2 + 5xH_2O \rightarrow yK^+ + M^{2+} + 2xRNH_2 + 6xH^+$$
$$+ \, xCNO^- + xSO_4^{2-} + 4xBr^-, \qquad (2)$$

where $y = 1$ and $x = 3$ for M = UO_2, $y = 2$ and $x = 4$ for M = Zn and Cd, $y = 4$ and $x = 6$ for M = Ni and Pb.

The oxidation of cyanides and cyanide complexes is represented by

$$M(CN)_x + (x/2)RNBr_2 + xH_2O \rightarrow M^{x+} + xCNO^- + (x/2)RNH_2$$
$$+ \, xH^+ + xBr^-, \qquad (3)$$

$$KAg(CN)_2 + RNBr_2 + 2H_2O \rightarrow K^+ + Ag^+ + 2H^+ + 2CNO^-$$
$$+ 2Br^- + RNH_2, \qquad (4)$$

$$K_2Zn(CN)_4 + 2RNBr_2 + 4H_2O \rightarrow 2K^+ + Zn^{2+} + 4H^+ + 4CNO^-$$
$$+ 4Br^- + 2RNH_2, \qquad (5)$$
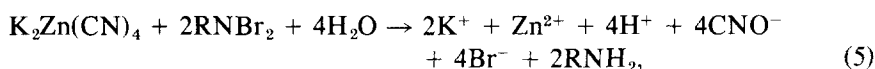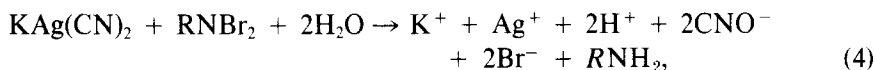
where $x = 1, 1,$ and 2 for sodium, potassium, and zinc cyanides, respectively. Similarly, the reactions, involving a 12-electron change per TSC ligand in the free state or in its metal complexes, with DBB may be represented by

$$H_2NNHCSNH_2 + 3RNBr_2 + 6H_2O \rightarrow 3RNH_2 + SO_4^{2-} + CO_2 + N_2$$
$$+ NH_4^+ + 7H^+ + 6Br^-, \qquad (6)$$

$$M(H_2NNHCSNH_2)_2X_2 + 6RNBr_2 + 12H_2O \rightarrow 6RNH_2 + M^{2+} + 2X^-$$
$$+ 2SO_4^{2-} + 2CO_2$$
$$+ 2N_2 + 2NH_4^+$$
$$+ 14H^+ + 12Br^-, \qquad (7)$$
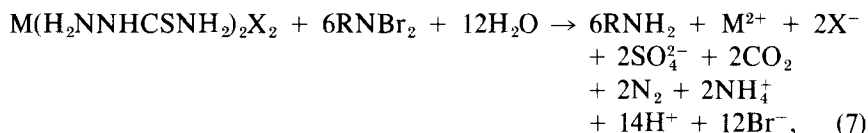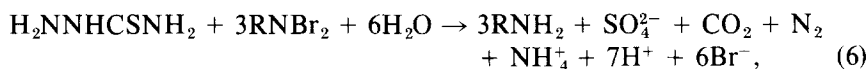
where $R = C_6H_5SO_2-$, $M =$ Zn, Ni, Cd, Hg, Pt, or Pd, and $X =$ Cl, Br, I, NO_3, ClO_4, or ½SO_4,
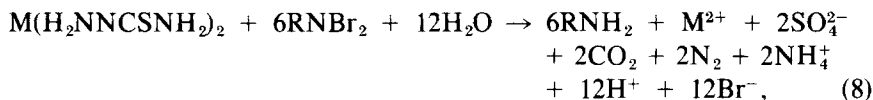
TABLE 3

ACCURACY AND REPRODUCIBILITY OF DETERMINATION OF THIOCYANATE AND
CYANIDE IONS IN METAL SALTS AND COMPLEXES WITH DIBROMAMINE-B (DBB)

Reductant	Amount taken (μmol)	SD[a] (μmol)	Coefficient of variance[a] (%)
LiNCS	117.7	0.020	0.20
NaNCS	140.0	0.020	0.20
KNCS	102.9	0.030	0.31
Zn(NCS)$_2$	52.6	0.001	0.01
Cd(NCS)$_2$	43.8	0.010	0.10
Ni(NCS)$_2 \cdot 0.5H_2O$	53.7	0.021	0.21
Ba(NCS)$_2 \cdot 2H_2O$	48.4	0.036	0.26
Pb(NCS)$_2$	27.5	0.016	0.18
UO$_2$(NCS)$_2 \cdot 3H_2O$	26.7	0.030	0.24
KUO$_2$(NCS)$_3 \cdot 2H_2O$	24.9	0.040	0.30
K$_2$Zn(NCS)$_4 \cdot 4H_2O$	25.0	0.026	0.23
K$_2$Cd(NCS)$_4 \cdot 2H_2O$	25.1	0.036	0.32
K$_4$Ni(NCS)$_6 \cdot 4H_2O$	15.0	0.010	0.12
K$_4$Pb(NCS)$_6$	15.0	0.007	0.06
NaCN	240.8	0.010	0.10
KCN	147.0	0.040	0.43
AgCN	99.7	0.010	0.08
Zn(CN)$_2$	87.3	0.040	0.41
KAg(CN)$_2$	51.4	0.010	0.11
K$_2$Zn(CN)$_4$	39.5	0.020	0.18

[a] Calculated for six trials.

$$M(H_2NNCSNH_2)_2 + 6RNBr_2 + 12H_2O \rightarrow 6RNH_2 + M^{2+} + 2SO_4^{2-}$$
$$+ 2CO_2 + 2N_2 + 2NH_4^+$$
$$+ 12H^+ + 12Br^-, \qquad (8)$$

where M = Ni, Pt, or Pd. Similar equations can be written for the oxidation of $Pt(H_2NNHCSNH_2)_2(NCS)_2$, $Pt(H_2NNHCSNH_2)_2(CN)_2$, and $Pd(H_2NNHCSNH_2)_2(NCS)_2$ by DBB.

In all the reactions studied, the oxidant undergoes a four-electron-change, with benzenesulfonamide as the reduction product. The products formed in the reactions do not undergo further oxidation.

Some typical results of analyses of thiocyanate and cyanide ions present in salts and complexes and thiosemicarbazide alone and in its metal complexes are given in Tables 3–6. The tables show the range of reductants employed, standard deviation, percentage coefficient of variance, and percentage error in recovery. Each range covers the sample sizes present in 8–10 different aliquots of the reductant solution. It is seen that the results are accurate within an error of about 0.7%.

Interference. Common anions such as SO_4^{2-}, PO_4^{3-}, NO_3^-, ClO_4^-, F^-, Cl^-, and Br^- do not interfere but hydrazine, urea, and thiourea interfere in the estimation.

TABLE 4
Determination of Thiocyanate and Cyanide Ions in Metal Salts and Complexes with Dibromamine-B

Reductant	Range studied (μmol)	Error in recovery (%)
LiNCS	23.53–588.30	0.26–0.00
NaNCS	28.00–700.01	0.40–0.00
KNCS	20.68–514.51	0.50–0.03
Zn(NCS)$_2$	10.52–263.04	0.17–0.00
Cd(NCS)$_2$	8.75–218.76	0.50–0.02
Ni(NCS)$_2\cdot$0.5H$_2$O	10.74–268.58	0.50–0.00
Ba(NCS)$_2\cdot$2H$_2$O	9.67–241.80	0.36–0.02
Pb(NCS)$_2$	5.51–137.62	0.50–0.02
UO$_2$(NCS)$_2\cdot$3H$_2$O	5.34–133.46	0.40–0.00
K$_2$Zn(NCS)$_4\cdot$2H$_2$O	5.00–125.03	0.45–0.00
K$_2$Cd(NCS)$_4\cdot$2H$_2$O	2.99–74.73	0.50–0.01
K$_4$Ni(NCS)$_6\cdot$4H$_2$O	2.99–74.78	0.47–0.01
K$_4$Pb(NCS)$_6$	4.99–124.67	0.40–0.00
NaCN	48.20–1204.10	0.01–0.00
KCN	29.33–734.79	0.63–0.00
AgCN	19.90–498.60	0.37–0.07
Zn(CN)$_2$	17.50–436.50	0.49–0.02
KAg(CN)$_2$	10.30–257.10	0.50–0.00
K$_2$Zn(CN)$_4$	7.90–197.30	0.50–0.01

TABLE 5

ACCURACY AND REPRODUCIBILITY OF DETERMINATION OF THIOSEMICARBAZIDE (L)
AND ITS METAL COMPLEXES WITH DIBROMAMINE-B

Complex	Reductant taken (μmol)	SD[a] (μmol)	Coefficient of variance[a] (%)
L	109.72	0.031	0.31
ZnL$_2$SO$_4$	28.65	0.050	0.51
ZnL$_2$Cl$_2$	30.07	0.063	0.67
ZnL$_2$(NO$_3$)$_2$	27.47	0.054	0.53
ZnL$_2$(ClO$_4$)$_2$	25.69	0.043	0.38
CdL$_2$SO$_4$	25.13	0.050	0.52
CdL$_2$Cl$_2$	29.16	0.031	0.29
HgL$_2$Cl$_2$	20.03	0.066	0.73
NiL$_2$SO$_4$·3H$_2$O	22.96	0.033	0.37
NiL$_2$(NO$_3$)$_2$	20.16	0.010	0.10
NiL$_2$Cl$_2$	31.85	0.060	0.60
Ni(L-H)$_2$	42.09	0.026	0.25
PdL$_2$Cl$_2$	24.75	0.037	0.41
PdL$_2$Br$_2$	21.05	0.040	0.43
PdL$_2$I$_2$	21.05	0.024	0.22
PdL$_2$(NCS)$_2$	22.23	0.044	0.49
cis-PdL$_2$(NO$_3$)$_2$	23.02	0.053	0.55
trans-PdL$_2$(NO$_3$)$_2$	23.02	0.053	0.55
Pd(L-H)$_2$	31.46	0.015	0.17
cis-PtL$_2$Cl$_2$	23.30	0.046	0.41
trans-PtL$_2$Cl$_2$	23.30	0.044	0.25
PtL$_2$Br$_2$	20.36	0.021	0.20
PtL$_2$I$_2$	28.34	0.020	0.20
PtL$_2$(CN)$_2$	23.99	0.021	0.20
PtL$_2$(NCS)$_2$	19.47	0.022	0.23
PtL$_2$(NO$_3$)$_2$	21.78	0.024	0.22
Pt(L-H)$_2$	20.41	0.022	0.29

[a] Calculated for six trials.

Product analyses. The presence of sulfate in the reaction mixture was detected (2) using sodium rhodizonate and barium chloride. Cyanate was identified by the Werner test (29) as follows: a few drops of pyridine and 2–3 drops of a 1% solution of copper sulfate were added to 10 ml of H$_2$O. Then 2 ml of chloroform was added followed by the test solution. On shaking the mixture briskly, a lilac blue color appeared in the chloroform layer due to the formation of the complex, Cu(CNO)$_2$(C$_5$H$_5$N)$_2$. Benzene-sulfonamide, the reduction product of DBB, was detected (30) by thin-layer chromatography. A mixture of petroleum ether, chloroform, and *n*-butanol (2:2:1, v/v) was used as the solvent (R_f = 0.88). Iodine was employed as the detection reagent.

It can be concluded that the proposed analytical procedures are simple,

TABLE 6
DETERMINATION OF THIOSEMICARBAZIDE (L) AND ITS METAL COMPLEXES
WITH DIBROMAMINE-B

Complex	Range studied (μmol)	Error in recovery (%)
L	21.94–548.60	0.03–0.50
ZnL$_2$SO$_4$	5.73–143.43	0.00–0.51
ZnL$_2$Cl$_2$	6.00–150.33	0.04–0.52
ZnL$_2$(NO$_3$)$_2$	5.49–137.31	0.00–0.33
ZnL$_2$(ClO$_4$)$_2$	5.13–128.43	0.00–0.58
CdL$_2$SO$_4$	5.02–125.66	0.00–0.51
CdL$_2$Cl$_2$	5.83–145.79	0.00–0.47
HgL$_2$Cl$_2$	4.01–100.11	0.00–0.55
NiL$_2$SO$_4$·3H$_2$O	4.60–115.07	0.00–0.59
NiL$_2$(NO$_3$)$_2$	4.03–100.82	0.00–0.60
NiL$_2$Cl$_2$	6.28–157.42	0.00–0.37
Ni(L–H)$_2$	8.41–210.38	0.00–0.50
PdL$_2$Cl$_2$	4.95–123.76	0.04–0.67
PdL$_2$Br$_2$	4.21–84.19	0.00–0.54
PdL$_2$I$_2$	4.11–82.42	0.00–0.63
PdL$_2$(NCS)$_2$	4.45–88.92	0.00–0.19
cis-PdL$_2$(NO$_3$)$_2$	4.60–92.08	0.00–0.53
trans-PdL$_2$(NO$_3$)$_2$	4.60–92.08	0.00–0.53
Pd(L–H)$_2$	6.28–125.85	0.00–0.56
cis-PtL$_2$Cl$_2$	4.66–116.56	0.10–0.48
trans-PtL$_2$Cl$_2$	4.66–116.56	0.10–0.48
PtL$_2$Br$_2$	4.06–81.42	0.00–0.46
PtL$_2$I$_2$	5.64–113.37	0.00–0.56
PtL$_2$(CN)$_2$	4.80–95.95	0.00–0.49
PtL$_2$(NCS)$_2$	3.89–77.85	0.00–0.35
PtL$_2$(NO$_3$)$_2$	4.35–87.12	0.00–0.46
Pt(L–H)$_2$	4.08–81.63	0.00–0.65

rapid, and reproducible and are useful for determining the reductants in solution and for computing the number of ligands present in the complexes.

SUMMARY

   Simple, rapid, and reproducible analytical procedures, for determining thiocyanate and cyanide ions in metal salts and complexes and thiosemicarbazide (TSC) in the free state and in its metal complexes, with the new oxidant, dibromamine-B (DBB), have been proposed. These procedures are also useful for computing the number of ligands present in the complexes. With DBB, CN$^-$, and NCS$^-$ ions and TSC undergo stoichiometric oxidations with 2-, 8-, and 12-electron changes per ion or molecule, respectively, in water–acetic acid medium. The reagent DBB has been prepared and characterized by elemental analyses and ir and FT-NMR-^{1}H and -^{13}C spectral data.

ACKNOWLEDGMENTS

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