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A. J. Bauman[a]; James H. Richards[ab]
[a] JET PROPULSION LABORATORY, PASADENA, CALIFORNIA [b] American Peace Corps, Kamaladi, Kathmandu, Nepal

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A Simple Electrostatic Model for the Chromatographic Behavior of the Primary Dithizonates

A. J. BAUMAN and JAMES H. RICHARDS*

JET PROPULSION LABORATORY
PASADENA, CALIFORNIA 91103

Summary

A simple electrostatic model of the reactive sites of primary metal dithizonates which fits their published chromatographic behavior is described. Coordination with a metal ion tends to increase the formal charge on the hindered imino hydrogens in the molecule. This increase is a function of the individual metal's Sanderson electronegativity. Plots of R_m vs. electronegativity are rectilinear, have the same form for all systems and adsorbents described, and place dithizonates of similar molecular geometry on separate curves. The results of this study suggest that the dithizonates are a heterogeneous group of compounds which differ in coordination configuration and geometry.

INTRODUCTION

A widely used quantitative analysis scheme (*1*) for about 23 trace metals in soils and waters is based on their selective extraction into halocarbons as neutral complexes with dithizone, 3-mercapto-1-5, phenylformazan. Selection through pH control and masking is required because the complexes have generally similar absorption spectra and because some metals form a primary (P) dithizonate at low pH and an additional quite different polymeric (*2*) secondary (S) form at higher pH.

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* Present address: c/o American Peace Corps, Kamaladi, Kathmandu, Nepal.

CHROMATOGRAPHY OF THE (P) DITHIZONATES

Many paper (*3*, *4*), column (*5*, *6*) and thin-layer chromatographic studies (*7–12*) have been made of the (P) forms, notably by Hranisavljevic-Jakovljevic and her associates, but the analytically unimportant (S) forms have received little attention. An efficient chromatographic separation of the dithizonates might form the basis of a rapid field analysis method for trace metals in polluted waters.

The order of migration of the complexes is generally invariant on the many types of nonactivated adsorbents used, though separation efficiency is quite sensitive to the water content of the adsorbent. This suggests that the order is determined chiefly by hydrogen-bonding: the order of the Cd and Ni complexes is reported to change during the course of chromatography on potassium citrate (*6*).

We know of no previous mechanistic attempts to explain the observed migration order: Cd, Co, Pb, Ni, Cu, Zn, Hg, Mn for oxidation state II and As, Sb, Bi, Au for state III (*11*, *12*).

The cause of this order, however, must involve to various degrees the following types of adsorbent-adsorbate interactions (*13*):

(a) The area required by the adsorbed dithizonate molecule.
(b) The intramolecular electronic interactions.
(c) The intramolecular steric interactions as affected by the coordination configuration about the metal.
(d) The presence of additional ligands, such as water, within the complexes.

We may expect that the chromatographic behavior of the dithizonates will be some function of these combined effects, best discussed in terms of the molecular structural parameters which are most readily obtained by x-ray crystallography.

CRYSTAL STRUCTURE: THE INFLUENCE OF METAL-HETEROATOM RING SIZE ON R_F

The (P) dithizonates are considered to consist of 5-membered chelate rings in which the metal is bonded to S and N atoms, as shown in Fig. 1 for the case of Cu(II) (*14*). The experimentally determined metal–sulfur bond lengths in these complexes are in the order Ni (2.14 Å),

TABLE 1

List of a Typical Set of R_F and R_m Values for Chromatographically Separated Dithizonates, Together with the Corresponding Metals, Their Atomic Numbers and Calculated Cation Electronegativities, and Calculated Sulfur–Metal Bond Lengths

Element	Atomic No.	S-metal bond (Å) Observed	S-metal bond (Å) Calculated	Cation[a] electronegativity, S_{cat}	R_F[b] × 100	R_m, calculated
Mn(II)	25	—	2.19	(8.05)	64	−0.25
Hg(II)	80	2.41	2.51	9.59	63	−0.23
Zn(II)	30	2.28	2.27	10.14	57	−0.12
Cu(II)	29	1.85	2.19	9.26	50	0
Ni(II)	28	2.14	2.17	(8.12)	43	0.12
Pb(II)	82	—	2.49	8.80	28	0.41
Bi(III)	83	—	2.48	14.26	26	0.45
Co(II)	27	—	2.18	(8.12)	19	0.63
Cd(II)	48	—	2.50	9.29	10	0.95

[a] Sanderson (*15*), calculated from data in Table 6-5, p. 77: values in parentheses are least certain.

[b] Takeuchi and Tsunoda (*8*): system is *m*-xylene/silica gel.

Cu (1.85 Å), Zn (2.28 Å), and Hg (2.41 Å), which is the same as that of their chromatographic migration order. The covalent bond length can be closely approximated in each case except that of copper by simple addition of the nonpolar covalent radii (*15*) of the elements listed in Table 1. The S—Cu value by analogy is in error and should be 2.19 Å. There is, however, no clear relationship between a typical set of chromatographic R_m values (*16*) and the calculated metal–sulfur (M—S) bond lengths. The metal-heteroatom ring size therefore has a strong but indirect influence on the chromatographic behavior of the complexes. Table 1 also shows the calculated M—S bond lengths and the R_m values (*8*) for a typical dithizonate chromatographic separation.

CRYSTAL AND INFRARED SPECTRAL EVIDENCE FOR GROUP HETEROGENEITY

The lattice structure in Fig. 1 is that of a square-planar complex and this is also true for Ni(II) (*17*) and to a lesser extent for Hg(II) (*18*).

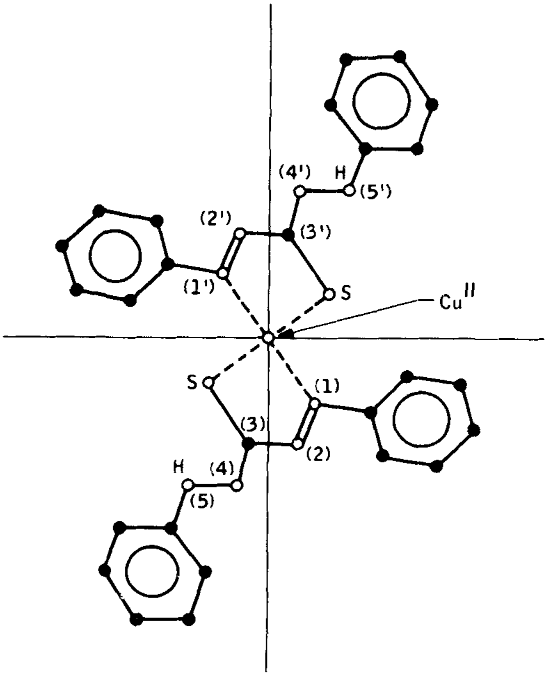

FIG. 1. Crystal structure of primary cupric dithizonate, as viewed down the short *c* axis (*14*). The full circles represent carbon atoms, the small open circles nitrogen, and the sulfurs and 5,5′ hydrogens are labeled.

The latter structure which contained pyridine of crystallization is that of a flattened tetrahedron with an S—Hg—S angle of 155°, an N—Hg—N angle of 102°, and an N—Hg—S angle of 70°. Thus, the complexes of Cu(II), Ni(II), and Hg(II) within the lattice are approximately flat and all ring systems are nearly coplanar. In zinc dithizonate, however, the Zn is tetrahedrally coordinated with each phenyl ring within the dithizonate moieties coplanar to its respective heteroatom ring (*19*). Thus, even the few x-ray structures reported to date suggest that the dithizonates exhibit structural variety.

This conclusion was reached independently by Laing and Alsop (*17*) who examined 14 dithizonate powders by means of x-ray diffraction. Only the complexes of Ni(II), Pd(II), and Pt(II) were structurally isomorphous, the others presumably being quite structurally heterogeneous. Meriwether, Breitner, and Sloan (*20*) is an IR study of 24 solid dithizonates classified the compounds into four groups on the basis of their spectral similarity. These were:

(1) $Mn(HDz)_2 \cdot H_2O$, $Zn(HDz)_2$, $Cd(HDz)_2$, $Hg(HDz)_2$, $SnO_2(HDz)_2 \cdot 2H_2O$, $Pb(HDz)_2$, and $Bi(HDz)_3$.
(2) $Cu(HDz)_2$ "brown", $AgHDz \cdot H_2O$, $Au(HDz)(OH)_2$, TlHDz.
(3) $Ni(HDz)_2$, $Pd(HDz)_2$ "green", $Pd(HDz)_2$ "red", $PdDz \cdot 2H_2O$, $Pt(HDz)_2$, $Cu(HDz)_2$ "violet."
(4) $Os(HDz)_3$, $Co(HDz)_2$.

Three others, $CuDz \cdot 2H_2O$, Ag_2Dz, and $Pd(HDz)_2$ "violet," had unique IR spectra unlike any of the others. In these formulae HDz is the dithizonate monoanion and the nonexistent dianion (*2*) characteristic of the (S) dithizonates is given as Dz.

Evidently the solid dithizonates are a structurally heterogeneous group of compounds, some of which contain water of coordination and some such as those with Pd which exhibit geometrical isomerism.

STERIC ARRANGEMENTS, HETEROGENEITY, AND PROTON ACIDITY

The varied intramolecular steric arrangements of the dithizonates must naturally affect the availability of the blocked 5,5′ (*21*) imino protons for hydrogen bonding as well as the orientation of the four peripheral phenyl groups for π-bonding. The formal charge on the imino protons must also affect their interaction with the weakly acidic positive surface fields (*13*) in the adsorbents used. This charge is determined by the electronegativity of the particular metal cation involved (*22*).

CATION ELECTRONEGATIVITY (S_{cat}) AND THE S_{cat}/R_m PLOT

Sanderson defines "electronegativity" (S_E) as that tendency of one atom in a covalent bond to acquire "most" of the electrons. Paradoxically, the most "electronegative" atom is that with highest formal positive charge. The change in electronegativity corresponding to acquisition of unit charge (+ or −) by some cation is easily calculated from the element electronegativities, S_E: $S_{E \to E\pm} = 2.08\ (S_E)^{1/2}$, where S_E is the electronegativity of atom E and 2.08 is an empirical constant. The electronegativity of a cation is then: $S_{cat} = S_E + n[2.08\ (S_E)^{1/2}]$, where n is

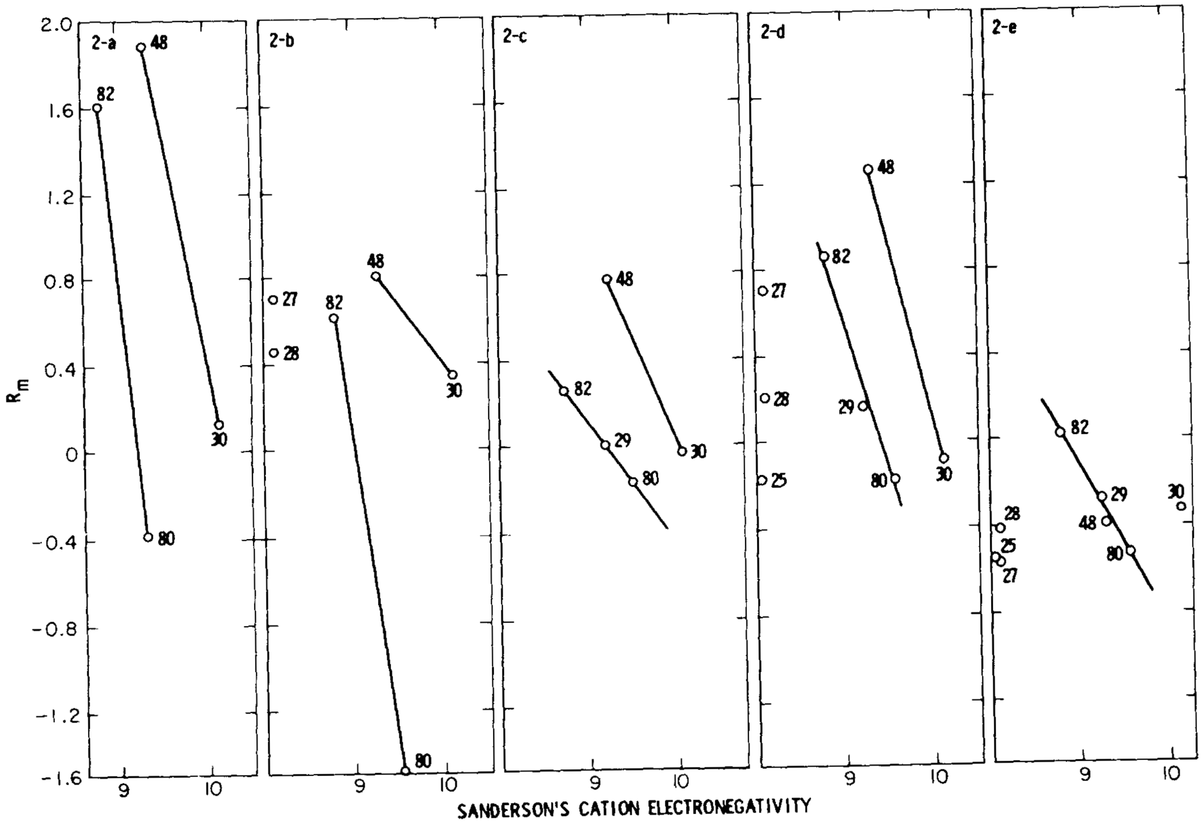

FIG. 2. Relationship between R_m and S_{cat} (for details, see text) for the following systems: 2a and 2b, data of Busev (*6*) for columns of sodium bicarbonate and potassium citrate, respectively, developed in carbon tetrachloride; 2c, data of Hranisavljevic-Jakovljevic (*9*) for TLC on silica gel G in methylene chloride:benzene 1:5; 2d and 2e, data of Takeuchi (*8*) for TLC on silica gel in *m*-xylene and on alumina in acetone, respectively. Complexed metals listed by atomic number.

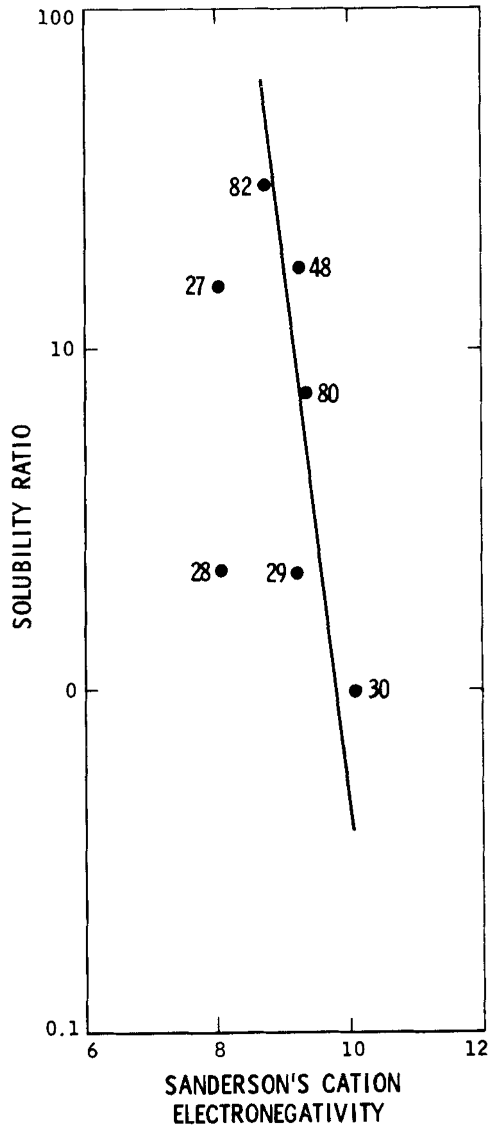

FIG. 3. Relationship between the ratio of dithizonate solubility in chloroform to that in carbon tetrachloride against S_{cat}. The data points were calculated from listed values in Iwantscheff (*23*) and the metals are listed according to atomic number.

the number of positive charges. Thus, for Zn as an example:

$$S_{\mathrm{E}}\mathrm{Zn}^{\circ} = 2.98$$

$$S_{\mathrm{cat}} = 2.98 + 2\,\{2.08(2.98)^{1/2}\} = 10.14$$

Table 1 also shows the calculated S_{cat} values for the dithizonate cations listed.

The plots of S_{cat} against R_m (elements marked by atomic number) shown in Fig. 2 have the same form for all data available, expect for variations in slope due to the adsorbent's water content. The plots show that tetrahedral Zn(II) and Cd(II) (probably tetrahedral) fall on one curve; the approximately square-planar Hg(II), Cu(II), and Pb(II) complexes on another; while a third group, Ni(II), Co(II), and Mn(II), exhibit deviant behavior. Solvent demixing effects (*16*) do not appear to perturb the form of the plot (Fig. 2c) or to affect the migration order. The quite similar curve shown in Fig. 3 results when the ratio of dithizonate solubility in chloroform relative to that in carbon tetrachloride (*23*) is plotted against S_{cat}. This ratio is a measure of the hydrogen-bonding tendency of the complexes and, as in the S_{cat}/R_m plots, Ni(II) and Co(II) again exhibit deviant behavior.

DISCUSSION

These plots of S_{cat} vs. R_m are consistent with a model of the dithizonate molecule as a simple ylidelike electrostatic dipole. The formal charge on the 5,5′-protons is determined by the extent of positive charge ("electronegativity") of the metal. Their H-bonding availability is modified by steric effects and internal bonding (*20*). These protons are not acidic and are not lost from dithizone, at least up to pH 14 (*24*). The model predicts that a set of dithizonates of equivalent molecular shape will migrate in the order of their increasing metal S_{cat} values. For example, the assumed nearly flat complexes of Pb(II), Cu(II), and Hg(II) migrate in an order which is consistent with the existing electrostatic repulsion between the 5,5′-protons and the adsorbent's positive surface field.

Considering that the S_{cat} values for Mn, Ni, and Co are somewhat uncertain, there is a remarkable consistency in the form of the S_{cat} vs. R_m plots shown in Fig. 2 for adsorbents as different as silicic acid, alumina, and potassium citrate. This again suggests that the adsorbents are nearly inert carriers for hydrogen-bonding surface water. One might have expected a different chromatographic order on π-bonding alumina.

The data scatter is less for associated solvents such as acetone (Fig. 2e) which not only would interact with bound water in the adsorbent (*25*) but which also would compete with coordinated water in the complexes. It is reasonable to assume that the dithizonates in solution are all solvated to some extent with water, as their photochromic return rates (*26*) are first-order with respect to water in the solvents used.

Few successful correlations have been made between the stability of a complex and some single property of the metal involved, as, for example, between log K and the ionization potential of the last electron to be lost. The Irving-Williams order (*27*) of increasing stability for divalent metals is the same as the order of their S_{cat} values: Mn, Fe, Co, Ni, Cu, Zn. Van Uitert, Fernelius, and Douglas (*28*) plotted the product: Pauling electronegativity times bond strength of hybrid orbitals against log K for a series of β-diketones with aromatic end groups. The order of increasing stability was Ba, Sr, Ca, Mg, Cd, Mn, Pb, Zn, Co, Ni, Fe, Cu = Be, Hg for these complexes. The S_{cat} relationship for the 5,5′-proton charge in the dithizonates does not agree well with the results of Harkins and Freiser (*29*) who studied the effect of metal coordination on the acidity of imino protons in 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imadazoline. The order of increasing cation effectiveness in increasing the imino acidity for these complexes was Mn, Ni, Zn, Co, and Cu, in approximate agreement with the results of Irving and Williams. Similarly, Bag, Fernando, and Freiser (*30*) showed an identical order for these metals in strengthening the acidity of the 4-hydroxyl group in a series of chelidamates.

The electrostatic model presented here for the interactions between the dithizonate reactive sites and the adsorbent is not, however, that of a classical Brönsted acid. Thus, it would predict the same chromatographic migration order for the imidazoles and chelidamates as for the dithizonates, with the same implied steric constraints. These compounds have not been chromatographed, nor have the dithizonates of Tl(I), Cu(I), Cu(I), and Au(I) which should migrate in that order, if our model is correct. It successfully predicts that As, Sb, and Bi dithizonates should migrate in the observed order (*12*) and its success in predicting the migration of similar sterically hindered complexes should be tested.

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REFERENCES

1. G. Iwantscheff, *Das Dithizon und seine Anwendung in der Mikro und Spurenanalyse*, Verlag-Chemie, Weinheim, Germany, 1958.
2. B. S. Freiser and H. Freiser, "On the Nature of the Enol or Secondary Series of Diphenylthiocarbazone Chelates," *Anal. Chem.*, *42*, 305 (1970).
3. O. Von Erametsa, "Die Chromatographie der Metalle als Diphenylthiocarbazonekomplexe," *Suomen Kemistilehti B*, *16*, 13 (1943); *Chem. Abstr.*, *40*, 4620.
4. G. Venturello and A. M. Ghe, "Chromatography of Organometallic Complexes: Dithizonates," *Anal. Chim. Acta*, *10*, 335 (1954).
5. R. O. Bach, "Nuevos Ensayos en Cromatografia Inorganica," *Ind. Quim.* (Buenos Aires), *12*, 301 (1950); *Chem. Abstr.*, *45*, 7463h.
6. A. I. Busev, I. P. Kharlamov, and O. V. Smirnova, "Chromatographic Separation of Dithizonates in the Determination of Microimpurities," *Zavod. Lab.*, *35*, 1301 (1969); *Chem. Abstr.*, *72*, 62420g.
7. Y. Nishimoto and S. Toyoshima, "Studies on Thin-Layer Chromatography of the Compounds Carrying Chelating Ability. III. Thin-Layer Chromatography of Organic Analytical Reagents. (II). Dithizone," *Yakugaku Zasshi*, *85*, 322 (1965); *Chem. Abstr.*, *63*, 12298d.
8. T. Takeuchi and Y. Tsunoda, "Thin-Layer Chromatography of Metallic Dithizonates," Nippon Kagaku Zasshi, *88*, 176 (1967); *Chem. Abstr.*, *66*, 121695b.
9. M. Hranisavljevic-Jakovljevic and I. Pejkovic-Tadic, "Thin-Layer Chromatography of Inorganic Ions. I. Separation of Metal Dithizonates," in *Thin-Layer Chromatography, Proceedings of a Symposium* (*Rome*) (G. B. Marini-Bettolo, ed.), Elsevier, New York, 1964, p. 223.
10. M. Hranisavljevic-Jakovljevic, I. Pejkovic-Tadic, K. Jakovljevic, and J. Miljkovic-Stojanovic, "Chromatography of Metal Dithizonates. II," *Srpsko Glasnik Khemdrushtva Beograd*, *29*(3), 115 (1964); *Chem. Abstr.*, *64*, 16599g.
11. M. Hranisavljevic-Jakovljevic, I. Pejkovic-Tadic, and J. Miljkovic-Stojanovic, "Thin-Layer Chromatography of Inorganic Ions. III. Separation of Some Noble Metal Dithizonates," *Mikrochim. Acta*, *1965*(1), 141.
12. M. Hranisavljevic-Jakovljevic and I. Pejkovic-Tadic, "Thin-Layer Chromatography of Inorganic Ions. IV. Separation of Arsenic, Antimony and Tin Dithizonates," *Mikrochim. Ichnoanalyt. Acta*, *5-6*, 936 (1965).
13. L. R. Snyder, *Principles of Adsorption Chromatography*, Dekker, New York, 1968.
14. R. F. Bryan and P. M. Knopf, "The Crystal Structure of Primary Cupric Dithizonate," *Proc. Chem. Soc.* (London), *1961*, 203.
15. R. T. Sanderson, *Inorganic Chemistry*, Reinhold, New York, 1967, p. 74.
16. E. Stahl, *Thin-Layer Chromatography*, Springer, New York, 1965, p. 103.

17. M. Laing and P. A. Alsop, "The Structure of Primary Nickel Dithizonate," *Talanta, 17,* 242 (1970).

18. M. M. Harding, "The Crystal Structure of the Mercury Dithizone Complex," *J. Chem. Soc., 1958,* 4136.

19. H. Freiser, *Talanta, 18,* 435 (1971).

20. L. S. Meriwether, E. C. Breitner, and C. L. Sloan, "The Photochromism of Metal Dithizonates," *J. Amer. Chem. Soc., 87,* 4441 (1965).

21. A. Janowski and T. Ganko, "The N—H Stretching Frequency in the Infrared Spectrum of Diphenylthiocarbazone (Dithizone)," *Bull. Acad. Pol. Sci., Ser. Sci. Chim., 16*(4), 223 (1968); *Chem. Abstr., 69,* 55850g.

22. R. T. Sanderson, *Chemical Bonds and Bond Energy,* Academic, New York, 1971.

23. Ref. 1, Table 4, p. 30.

24. R. W. Geiger and E. G. Sandell, "Copper(II)-Dithizone Equilibria in Water–Carbon Tetrachloride," *Anal. Chim. Acta, 8,* 197 (1953).

25. J. H. Pickett, C. H. Lochmuller, and L. B. Rogers, "Nuclear Magnetic Resonance Measurements of Line Width, Chemical Shift, and Intensity for Molecules Adsorbed on Silica," *Separ. Sci., 5,* 23 (1970).

26. L. S. Meriwether, E. C. Breitner, and N. B. Colthup, "Kinetic and Infrared Study of Photochromism of Metal Dithizonates," *J. Amer. Chem. Soc., 87,* 4448 (1965).

27. H. Irving and R. J. P. Williams, "Order of Stability of Metal Complexes," *Nature, 162,* 746 (1948).

28. L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, "Studies on Coordination Compounds. IV. A Comparison of the Chelating Tendencies of β-Diketones toward Divalent Metals," *J. Amer. Chem. Soc., 75,* 2736 (1953).

29. T. R. Harkins and H. Freiser, "The Effect of Coordination on Some Imidazole Analogs," *J. Amer. Chem. Soc., 78,* 1143 (1956).

30. S. P. Bag, Q. Fernando, and H. Freiser, "The Influence of Metal Chelation on the Structure of Chelidamic Acid," *Inorg. Chem., 1,* 887 (1962).

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