typically "covalent" and typically "ionic" compounds come so close to fitting the same simple relationship involving bond strength. One of the most uncertain aspects of the estimation of partial charge using the concept of electronegativity equalization has always been the arbitrary nature of the choice of 75% ionicity for an isolated molecule of NaF. Although this value has seemed reasonable in the light of measured dipole moments of diatomic molecules, which agree as well as might be expected with values calculated from partial charge,[10] and although its absolute accuracy is unimportant in the majority of applications where *relative* charge values permit all manner of useful comparisons, insights, and interpretations,[11] nevertheless it results in partial charges for atoms in "ionic" compounds that are far removed from the ionic charges that, even though polarization effects are considered, are implicit in accepted theory. For example, the partial charge estimated for chlorine in $MgCl_2$ is −0.28 instead of −1.00; in CaO the partial charge on oxygen is −0.57 instead of −2.00. What is the significance of this discrepancy?

Some light is directed on this question by recognition of the fundamental qualities of ions with respect to electron donor–acceptor interaction. For a cation certainly has the requisites of an electron acceptor, and a simple anion always has an outer shell of electron pairs readily available for sharing because of the high negative charge on the atom. Donor–acceptor interaction therefore seems inevitable when cations and anions are in such close contact as they are in a crystal. The extent to which such interaction exists may be related to the partial charges. Consistent with this view are the facts that (1) a negatively charged atom improves as donor as it becomes more negative,[12] and (2) the coordination number of the negative atom in a crystal increases with higher negative charge. This relationship is illustrated by the data for fluorides in Table II. To account for the common coordination of six or eight atoms around one which has only four outermost orbitals, we need only to recognize the resonance principle[13] that greater stability results from a larger number of partial bonds, where possible, than from an equivalent number of two-electron bonds.

TABLE II

RELATION OF COORDINATION NUMBER OF FLUORINE TO ITS PARTIAL CHARGE

Compd.	δ_F	C.N.	Compd.	δ_F	C.N.
CsF	−0.89	6	CaF_2	−0.47	4
RbF	−0.88	6	MgF_2	−0.34	3
KF	−0.85	6	BeF_2	−0.29	2
NaF	−0.75	6	AlF_3	−0.24	2
LiF	−0.74	6	BF_3	−0.19	1
BaF_2	−0.56	4	SiF_4	−0.17	1
SrF_2	−0.51	4	CF_4	−0.09	1

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RECEIVED FEBRUARY 3, 1964

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(10) Reference 1, p. 45.

(11) R. T. Sanderson, "Chemical Periodicity," Reinhold Publishing Corp., New York, N. Y., 1960.

(12) Reference 1, pp. 56 *et seq.*, 105, 169, 228, 249.

(13) R. E. Rundle, *J. Chem. Phys.*, **17**, 671 (1949); R. T. Sanderson, *J. Chem. Educ.*, **38**, 382 (1961).

Metal Ion Induced Rearrangements

Sir:

The condensation of α-amino-β-thiols with dicarbonyl compounds does not lead to the Schiff bases which would be good tetradentate metal chelating agents, but instead results largely in the formation of thiazolidines (with β-mercaptoalkylamines) or benzothiazolines (with *o*-aminobenzenethiols).

Thompson and Busch[1] prepared tetradentate ligands in the form of nickel(II) chelates in high yields by the reaction of a mixture of 2-aminoethanethiol, α-diketone, and a nickel salt.

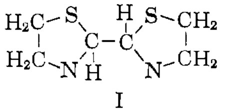
These authors assumed that the nickel ion influenced the condensation reaction by acting as a template, thus inhibiting the formation of thiazolidines. They did not consider the possible reaction of the thiazolidine with the metal ion to give the metal chelate. It has been reported, however, that 2,2′-bisbenzoxazolinyl rearranges in the presence of metal ions to give the corresponding Schiff base chelates.[2] It was therefore decided to determine whether bisthiazolinyls would undergo similar metal ion induced rearrangements.

For this purpose we have prepared the following three compounds, which are stable, white crystalline solids, by the condensation of glyoxal or diacetyl with 2-aminoethanethiol or *o*-aminobenzenethiol.

(I) 2,2′-Bisthiazolidinyl (m.p. 179–181° dec.). *Anal.* Calcd.: C, 40.87; H, 6.86; N, 15.89; S, 36.37. Found: C, 41.17; H, 6.38; N, 14.88; S, 38.72.

(II) 2,2′-Bisbenzthiazolinyl (decomposes above 160°). *Anal.* Calcd.: C, 61.71; H, 4.43; N, 10.29; S, 23.56. Found: C, 62.0; H, 4.0; N, 10.0; S, 22.7.

(III) 2,2′-Dimethyl-2,2′-bisbenzthiazolinyl (m.p. 149–150°). *Anal.* Calcd.: C, 63.96; H, 5.37; N, 9.33; S, 21.35. Found: C, 64.15; H, 5.37; N, 9.37; S, 21.39.



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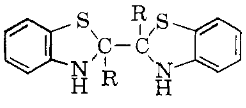

II, R = H
III, R = CH_3

Of these compounds, only II has been reported previously,[3] but this (brownish crystals, m.p. 283°) was probably the oxidation product, 2,2′-bisbenzthiazolyl.

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(1) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **84**, 1762 (1962).

(2) E. Bayer and G. Schenck, *Ber.*, **93**, 1184 (1960).

(3) M. Claasz, *ibid.*, **49**, 1141 (1916).

When these stable compounds were heated with certain metal acetates in organic solvents, highly colored crystalline chelates were obtained.

Compound I reacts with nickel(II) to give a deep violet complex(IV) which is soluble in organic solvents. The visible spectrum of this complex in chloroform closely resembles that of the dimethyl derivative prepared according to the method of Thompson and Busch.[1] Like biacetylbis(mercaptoethylimine)nickel(II), compound IV displays a weak absorption band at 430 mμ. Another, more intense band is exhibited at 565 mμ which is analogous to the 550 mμ band observed in the nickel(II) complex of the dimethyl derivative.

Compound II gives blue or blue-black crystalline chelates with cadmium(II) and zinc(II) which are soluble in dimethylformamide, dimethyl sulfoxide, and pyridine and give blue-violet or blue solutions. The infrared spectra of these zinc and cadmium chelates are very similar. The visible spectrum of the zinc chelate in dimethylformamide has two absorption bands at 370 and 560 mμ and the absorption bands of the cadmium chelate are observed at 360 and 540 mμ.

Compound III gives orange-red crystalline chelates with cadmium(II) and zinc(II) whose infrared spectra are very similar and which are soluble in dimethylformamide, dimethyl sulfoxide, and pyridine and give yellow or red solutions. In dimethylformamide the zinc chelate has an absorption band at 470 mμ and the cadmium chelate has one at 440 mμ.

The analyses of these metal chelates correspond to a metal:ligand ratio of 1:1.

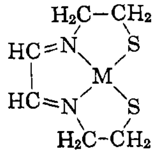
Glyoxalbis(2-mercaptoanil)cadmium(II): *Anal.* Calcd.: C, 43.93; H, 2.63; N, 7.32; S, 16.75; Cd, 29.37. Found: C, 43.98; H, 3.03; N, 7.15; S, 16.72, Cd, 28.47.

Diacetylbis(2-mercaptoanil)zinc(II): *Anal.* Calcd.: C, 52.82; H, 3.88; N, 7.70; S, 17.6. Found: C, 53.00,; H, 4.35; N, 7.65; S, 17.44.

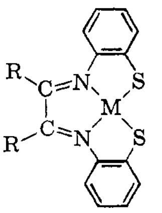
Diacetylbis(2-mercaptoanil)cadmium(II): *Anal.* Calcd.: C, 46.78; H, 3.44; N, 6.82. Found: C, 46.88; H, 3.80; N, 6.53.

Glyoxalbis(2-mercaptoanil)zinc(II): *Anal.* Calcd.: C, 50.08; H, 3.00; N, 8.34. Found: C, 50.07; H, 3.28; N, 8.08.

Thus the structures of the chelates obtained correspond to the Schiff base complexes IV, V, and VI.

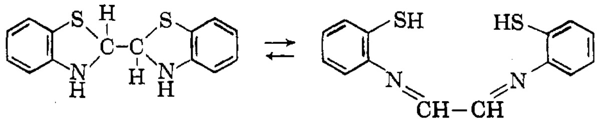


IV



V, R=H
VI, R=CH₃

The rate of formation of the colored chelate from compound II and zinc(II) or cadmium(II) in dimethylformamide solution at room temperature was followed spectrophotometrically. In the concentration range studied (2.5×10^{-4} *M* compound II and 5×10^{-2} to 1×10^{-4} *M* zinc(II)) the rate of chelate formation of compound II with zinc(II) is zero order with respect to the metal ion, but with cadmium(II) it is essentially first order (0.8) with respect to the metal ion in the concentration range 5×10^{-5} to 5×10^{-4} *M* cadmium(II) and 2.5×10^{-4} *M* compound II. Thus, although a metal complex of the same general structure is formed in both cases, the course of the reaction is seen to depend on the metal ion involved. The rate-determining step in the reaction of compound II with zinc(II) is probably the formation of the Schiff base tautomer.



On the other hand, the reaction of compound II with cadmium(II) proceeds *via* a direct attack of the thiazoline by the metal ion. These results show that the metal ion need not necessarily act as a template in the formation of chelates which are homologs of biacetylbis(mercaptoethylimine)nickel(II).

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Received February 11, 1964

Structure in the Electronic Spectra of Vanadyl Acetylacetonate

Sir:

A recent communication[1] of structure in the visible spectrum of some vanadyl complexes at low temperature in glassy solution prompts us to communicate some observations on structure in the low-temperature spectrum of single crystals of vanadyl acetylacetonate. Figure 1 shows that we have been able to resolve the structure in three regions in the spectrum of vanadyl acetylacetonate. In the first region, the visible, and the third region, occurring at about 25 kK., structure appears which can be interpreted as a progression of a vibrational mode of frequency about 0.7 kK. We are tempted to assign this vibrational mode to the vanadyl stretching frequency which in the ground state occurs at about 0.99 kK.[2] If our interpretation of the structure is correct, then excitation in both the 14 and 25 kK. regions must involve a considerable change in the electronic structure of the vanadyl group itself. This can be a clue to assignment of the 25 kK. band as a charge-transfer band or a vanadyl internal transition

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[1] J. Selbin, T. R. Ortolano, and J. F. Smith, *Inorg. Chem.*, **2**, 1315 (1963). (See here also the many references to vanadyl spectroscopy.)

[2] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 4533 (1961).