oxygen to substrates, yet it can release oxygen in a probable photochemical bimolecular reaction. Scheme I is a summary of our photochemical results with dilute and concentrated suspensions of Cp_2MoCO_3 and of other known reactions in the literature.[19-21] The photolysis of dilute suspensions of Cp_2MoCO_3 involves several pathways. One pathway gives only $Cp_2Mo{=}O$ (there is some unreacted Cp_2MoCO_3 when the photolysis time is very short). No oxygen or carbon monoxide is detected in the gas phase. The second pathway we propose is that if any oxygen is produced either from cleavage of Cp_2MoCO_3 or more likely from $Cp_2Mo{=}O$, it interacts with **5** to re-form **1**. We propose that **5** is produced from the reaction of "Cp_2Mo" with CO_2 that is generated from the initial decomposition of Cp_2MoCO_3. Thus no CO- or MoCO-containing products will be observed when dilute suspensions of Cp_2MoCO_3 are photolyzed less than 2 h. A combination of different kinetics and different amounts of material produced preclude the formation of oxygen and carbon monoxide at short photolysis times, cf. Scheme I. After photolysis of dilute suspensions for 1 h, the UV spectrum of the green solution showed that some Cp_2MoCO_3 remains along with the $Cp_2Mo{=}O$ that is formed. After 2 h of photolysis and Cp_2MoCO_3 concentrations of up to 4 mg/10 mL of THF, no Cp_2MoCO_3 is left, and the solutions are clear green.

The photolysis of more concentrated suspensions of Cp_2MoCO_3 in THF shows the presence of small ratios of oxygen and carbon monoxide. These gases are formed because more starting material is present than can be photolyzed and secondly because "Cp_2Mo" can form a complex with CO_2 to form Cp_2MoCO_2,[20] which in turn can form Cp_2MoCO,[21] just as it does with dilute suspensions. The ratio of oxygen is low because most of it is being consumed in the side reaction of Cp_2MoCO_3 regeneration or interaction with $Cp_2Mo{=}O$.[19] If there were no CO_2 present, then the amount of oxygen would be substantial as Tyler[19] reports with just photolysis of $Cp_2Mo{=}O$ alone.

Conclusion

Photochemical fragmentation of an early-transition-metal carbonate generates carbon dioxide and the metallo–oxo complex $Cp_2Mo{=}O$. More concentrated suspensions generate oxygen gas.

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Contribution from the Loker Hydrocarbon Research Institute,
Department of Chemistry, University of Southern California,
Los Angeles, California 90089-1661,
and Department of Chemistry,
Dalhousie University,
Halifax, Nova Scotia, Canada, B3H 4J3

A New Electronegativity Scale. 12. Intrinsic Lewis Acid Strength for Main-Group Elements

Yu-Ran Luo[†] and Sidney W. Benson*[,‡]

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We have recently discovered a good linear relation, (Figure 1) between the new electronegativity scale, V_X, and Brown's scale of Lewis acid strength, S_a, for 28 main-group elements in their highest oxidation state. This new V_X scale was found to give the best correlation for S_a in a comparison with other available electronegativity scales.

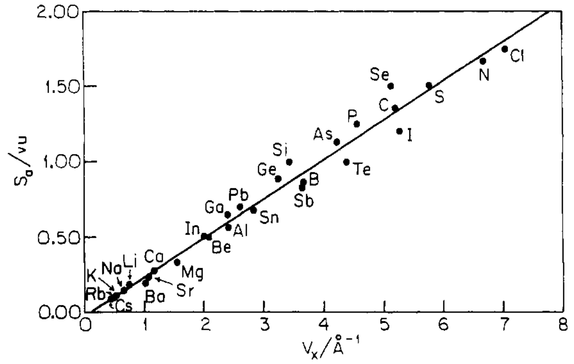

Figure 1. Relation between the new scale of electronegativity[5] and Lewis acid strengths[1] of main-group elements.

Table I. Correlation Coefficients of Lewis Acid Strengths with Various Electronegativities

rank order	scales	correln coeff
1	Luo-Benson[5]	0.9906
2	Zhang[16]	0.9839
3	Allred-Rochow[17]	0.9803
4	Boyd-Markus[18]	0.9778
5	Allen[19]	0.9764
6	Pauling[20]	0.9755
7	revised Mulliken[21]	0.9355

Very recently, inorganic crystal structures for over 14 000 coordination environments involving nearly 100 different cations were analyzed by Brown.[1] The average coordination number to oxygen observed in a large sample of compounds, N_t, was used to calculate a scale of cation Lewis acid strengths, S_a, i.e.

$$S_a = V/N_t \tag{1}$$

where S_a is in valence units (vu), which represents the electron pairs per bond, and V is the oxidation state of the cation. There are linear relations[1,2] between Brown's scale of Lewis acid strength and some scales of electronegativity, such as Zhang's X_Z, Allred-Rochow's, X_{AR},[1] and Allen's, X_A, scales:

$$X_Z = 1.18S_a + 0.771 \tag{2}$$

$$X_{AR} = 4.90S_a \tag{3}$$

$$X_A = (S_a/1.18)^{0.5} \tag{4}$$

The values of S_a allow one to predict which Lewis acids will bond to which Lewis bases using the observation that both numerical strengths must be equal for maximum bonding.

We have reported a new scale of electronegativity.[3,4] This scale gave the least scatter and the highest correlation coefficient with heats of formation of alkyl derivatives of main-group elements.[5] It has been used very satisfactorily for estimating heats of formation of different alkyl derivatives,[3,4] group parameters for additivity schemes, ionization potentials of main-group atoms,[7] thermochemistry of silicon-containing compounds,[8] homopolar

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[†] Dalhousie University.

[‡] University of Southern California.

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bond dissociation energies,[9-11] the propagator of the σ inductive effect,[1,10] heteropolar bond dissociation energies,[12] and bond energies of silicon compounds[8,13] and for proposing a theoretical model of bond fissions.[14] We have found that our new scale also correlates very well with the intrinsic Lewis acid strengths S_a. Table I gives the correlation coefficients for the seven best electronegativity models useful for the description of the intrinsic Lewis acid strengths. Among these it can be seen that our new scale gives the best correlation.

The linear equation in Figure 1 can be described by

$$S_a = -0.0207\ (\pm 0.0241) + 0.260\ (\pm 0.00676) V_X \tag{5}$$

or be well approximated as

$$V_X = 4S_a \tag{6}$$

It may be noted that the new electronegativity V_X scale gives excellent correlations with the energetic properties of polyatomic molecular systems, such as heats of formation, ionization potentials, Lewis acid strengths, and homopolar and heteropolar bond dissociation energies. Is there any reason for this?

There are over 20 available scales, including Pauling and Pauling-like semiempirical, nonempirical, and absolute scales, of atom electronegativity at present. All scales agree in the essential ordering of the elements in the periodic table. In this view, the periodic table itself may be considered the first and best table of atom electronegativity. One of the goals in developing an electronegativity theory is to correlate quantitatively with known properties so as to predict unknown properties.

Our electronegativity V_X is the core-shielded electrostatic potential of X at the covalent radius of X.[5] It was termed the covalent potential and was defined as the ratio between the number of valence electrons in the bonding atom in the atom or group X, n_X, and its covalent radius, r_X. Since the outermost or valence electrons of an atom are directly involved in chemical bonding, the chemical properties of an atom are the properties of its outermost or valence electrons at the bonding (covalent or ionic) distance. Consequently, the covalent potential should be a most basic parameter for the contributions of atoms to molecular properties.

Very recently, Luo and Pacey have pointed out[15] that a powerful theoretical support of the new electronegativity scale came from Parr–Pearson absolute electronegativity theory.[22] In this theory, r_m, the radial distances at which the electrostatic potential of the ground-state atoms do exactly equal their chemical potentials, and the covalent radii of the atoms in molecules are close to each other.[23] Any atom in a molecule is in its energetically optimum valence state. Luo and Pacey have found that the chemical potentials of an atom in both its free ground state and in its valence state correlate very well with the new scale of electronegativity.[15] This fact suggests that the new scale is theoretically reasonable.

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Contribution from the Department of Chemistry
and Biochemistry, Sinsheimer Laboratories, University
of California, Santa Cruz, California 95064,
and Department of Chemistry, University
of California, Davis, California 95616

Synthetic Analogue Approach to Metallobleomycins: Possibility of Coordination of the Carboxamide Group of the β-Aminoalaninamide Moiety of Bleomycin to Copper in Copper(II) Bleomycin at Physiological pH

Larry A. Scheich,† Patricia Gosling, Steven J. Brown,
Marilyn M. Olmstead, and Pradip K. Mascharak*

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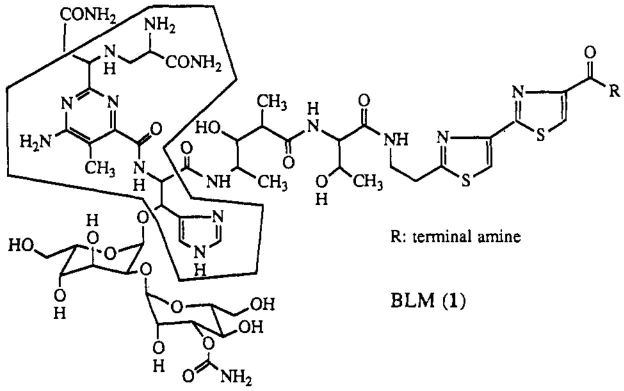
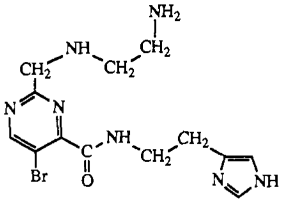
Introduction

The antineoplastic action of the bleomycin (BLM, **1**) family of antibiotics is attributed to the oxidative damage of cellular DNA by the metal chelates (metallobleomycins, M-BLMs) of the drugs.[1]

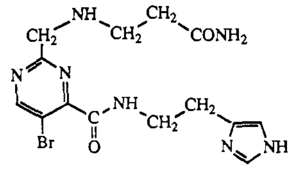


R: terminal amine

BLM (**1**)



PMAH (**2**)



PMBH (**3**)

Elucidation of the exact mechanism of the O_2-activation and concomitant DNA strand scission by M-BLMs therefore requires precise structural data on the metallated drugs. It is quite unfortunate that, to date, no M-BLM has been characterized by crystallography. The coordination structures of M-BLMs have been predicted primarily on the basis of spectroscopic data. Reports on the synthetic analogues of M-BLMs[2-4] are also no exception.

As part of our systematic analogue approach to M-BLMs, we have recently reported the structures and properties of the Cu(II) and Co(III) complexes of the designed ligand PMAH (**2**; the dissociable H is the amide H), which mimics a major portion of the metal-chelating locus of BLM.[5-7] The spectral parameters[5] as well as the characteristics of the DNA cleavage reaction[6] by [Cu(II)-PMA]X (X = ClO_4^-, BF_4^-) have established the architecture of the coordination sphere of copper in Cu(II)-BLM. Comparison of PMAH (**2**) with the metal-chelating portion of BLM (boxed area in **1**) reveals that the amide group of the β-aminoalaninamide part of BLM is not modeled in this designed ligand. In order to check the possibility (and the consequence(s)) of coordination of this primary amide group to metals in M-BLMs, we have completed the synthesis of a second designed ligand PMBH (**3**; the dissociable H is the secondary amide H, i.e. the

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* To whom correspondence should be addressed at the University of California, Santa Cruz.

† Permanent address: St. Norbert College, De Pere, WI 54115-2099.

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